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Learning about epoxy cure mechanisms from isoconversional analysis of DSC data

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Abstract

Model-free isoconversional methods can be effectively applied to isothermal and non-isothermal differential scanning calorimetry (DSC) data on epoxy cures. These methods yield a dependence of the effective activation energy on the extent of cure. Analysis of this dependence allows for untangling complex cure processes that may include different chemical reactions or a chemical reaction complicated by a mass transfer processes such as viscous relaxation and vitrification. The applications are illustrated by simulations as well as by epoxy-anhydride and epoxy-amine cures. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The epoxy cure kinetics are conveniently monitored by differential scanning calorimetry (DSC). The heat flow measured in DSC is proportional to both overall heat release and cure rate:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = Q_{\mathrm{rxn}}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Q_{\mathrm{rxn}}k(T)f(\alpha) \quad (1)$$

where $\mathrm{d}Q/\mathrm{d}t$ is the heat flow, Q_{rxn} the total heat released when an uncured material is brought to complete cure, $\mathrm{d}\alpha/\mathrm{d}t$ the cure rate, α the extent of cure, $k(T)$ the rate constant, T the temperature, and $f(\alpha)$ is the reaction model. For epoxy cures, $f(\alpha)$ is usually taken in the form of $(1-\alpha)^n$ (reaction order kinetics) or of $\alpha^m(1-\alpha)^n$ (autocatalytic cure). The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

where A is the pre-exponential factor, E the activation energy, and R is the gas constant. When a sample is heated at a constant rate, the explicit temporal dependence in Eq. (2) is eliminated through the trivial transformation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (3)$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate. For both isothermal and non-isothermal conditions, the extent of cure, α is estimated by integrating DSC peaks.

There are two major approaches to kinetic analysis [1]. The first approach is based on fitting of kinetic

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data to assumed reaction models. Most commonly the data are fitted to a single-step reaction model that obviously yields a single averaged value of the activation energy for the overall cure process. The resulting value does not reflect changes in the reaction mechanism and kinetics with the temperature and the extent of conversion [2]. However, epoxy cures are known to involve multiple steps that are likely to have different activation energies. The reaction complexity is accounted for by using more complex models such as that of Kamal [3]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = [k_1(T) + k_2(T)\alpha^m](1-\alpha)^n \tag{4}$$

Unfortunately, the standard model-fitting techniques do not appear to be very effective in detecting this type of curing reaction complexity [2]. Besides, when applied to non-isothermal single heating rate data, this approach tends to produce rather uncertain values of the activation energy, which cannot be meaningfully compared with the isothermal values [2].

An alternative approach is to use the model-free isoconversional methods [1]. Without assuming a particular form of the reaction model, these methods allow for evaluating the effective activation energy as a function of the extent of cure. The model-free kinetics of epoxy cures have been a subject of our collaborative research effort since 1995. The reader may be familiar with some pieces of this research that have been scattered since then over several of our prepublications and presentations at conferences. This paper pastes the pieces together in order to demonstrate the versatility of the model-free kinetic analysis as it applies to the reactions of epoxy cures. In particular, we demonstrate that this type of analysis allows one not only to obtain consistent results from isothermal and non-isothermal data, but also to get important clues about the cure mechanisms. We, therefore, hope that this paper will be helpful as a practical introduction to the model-free analysis of the epoxy cure kinetics.

2. Experimental

An epoxy-anhydride system was a mixture of DGEBA of MW $\sim 348\ \mathrm{g\,mol^{-1}}$ with hexahydro-4-methylphthalic anhydride (HHMPA). *N*,*N*-dimethylbenzylamine (DMBA) was used as an initiator. The system was cured under non-isothermal conditions at heating rates 1, 2, 3, and 4 $^\circ\mathrm{C\,min^{-1}}$ and isothermal conditions at temperatures 65, 70, 80, 90, and 100 °C, respectively which are below the experimentally determined value of the limiting glass transition temperature, $T_{\mathrm{g},\infty} = 110\ ^\circ\mathrm{C}$. An epoxy-amine system was a mixture an epoxy novolac containing 1,4-butanediol diglycidic ether (Araldite LY 5052) with an isophorone diamine (Araldite HY 5052). The DSC runs were carried out at heating rates 1, 2, 3, 4, and 5 $^\circ\mathrm{C\,min^{-1}}$ and under isothermal conditions at temperatures 40, 60, 80, 100 and 120 °C, respectively which are below $T_{\mathrm{g},\infty} = 126\ ^\circ\mathrm{C}$. A Setaram DSC-111 and Mettler-Toledo DSC-821$^\mathrm{e}$ were used to follow the cure kinetics under both non-isothermal and isothermal conditions. Samples of about 60–100 mg for DSC-111 and of about 5–10 mg for DSC-821$^\mathrm{e}$ were examined in pierced aluminum pans sealed under argon.

3. Isoconversional methods

If changes in the mechanism are associated with changes in the activation energy, they can be detected by using the model-free isoconversional methods [2]. These methods are based on the isoconversional principle that states that the reaction rate at constant extent of conversion is only a function of the temperature:

$$\left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}T^{-1}}\right]_\alpha = -\frac{E_\alpha}{R} \tag{5}$$

henceforth, the subscript α indicates the values related to a given extent of conversion. This statement holds strictly only when $f(\alpha)$ is independent of T which is the case of a single-step reaction. For multi-step kinetics, the global value of α does not uniquely determine the composition of the reacting system. This ultimately causes E_α to vary with α that reflects the variation in relative contributions of single-steps to the overall reaction rate.

To estimate the E_α-dependencies for epoxy cures, we used the advanced isoconversional method developed by Vyazovkin [4,5]. According to this method, for a set of n experiments carried out at different arbitrary heating programs, $T_i(t)$ the activation energy is determined at any particular value of α by finding the value of E_α that minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{6}$$

In Eq. (6), the integral

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_0^{t_\alpha}\exp\left[-\frac{E_\alpha}{RT_i(t)}\right]\mathrm{d}t \tag{7}$$

is evaluated numerically for a set of experimental heating programs. The minimization procedure is repeated for each value of α to determine the E_α-dependence. The advantage of the advanced isoconversional method is that it applies the same computational algorithm to both isothermal and non-isothermal DSC data. Note that in the case of a strong variation in E_α the integral in Eq. (7) should be carried out over small segments $\Delta\alpha$:

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha}\exp\left[-\frac{E_\alpha}{RT_i(t)}\right]\mathrm{d}t \tag{8}$$

in order to eliminate the accumulation of a systematic error in E_α [5].

4. Mechanistic conclusions

The process of an epoxy-anhydride cure provides a good example of the mechanistic interpretation of an E_α-dependence. The application of Eq. (6) to the cure data gives rise to an increasing E_α-dependence (Fig. 1). The occurrence of this dependence immediately suggests that the examined epoxy-anhydride cure follows multi-step kinetics. According to our previous studies [6], this type of the E_α-dependence is characteristic of a reaction mechanism that involves simultaneous channels with the respective activation energies of about 20 and 70 kJ mol^{-1}. This scheme can be interpreted as follows. The cure is initiated by a reaction of the tertiary amine with the epoxy group to produce a zwitterion, the alkoxide anion of which quickly reacts with the anhydride to form the carboxy anion. The latter opens the epoxy ring producing a new alkoxide anion. This alternating anionic copolymerization controls propagation of the polymer chain. The mechanism for this major channel was first proposed by Matejka et al. [7]. Trappe et al. [8] found that the initiation rate is significantly slower than the rate of propagation. Assuming that the initial stages of epoxy-anhydride cure are controlled by initiation, we may assign the value of 20 kJ mol^{-1} to the activation energy of initiation. To test this hypothesis, we evaluated the activation energy for the cure process in the system without HHMPA. This process has the same initiation step as the original system, but different mechanism of propagation [9]. As seen in Fig. 1, the process of cure in the system without the anhydride has a practically constant activation of energy of about 20 kJ mol^{-1}. The agreement of the activation energies of the initial stages of cure in both systems suggests that 20 kJ mol^{-1} is indeed the activation energy of initiation. The activation energy of 70 kJ mol^{-1} should then be assigned to the process of propagation of the polymer chain. Therefore, the increasing E_α-dependence (Fig. 1) represents a quickly growing contribution of the propagation process to the overall cure rate.

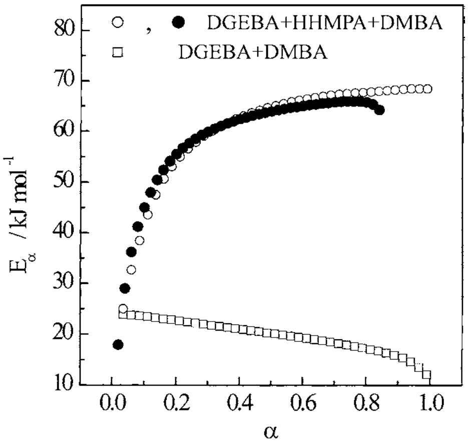

Fig. 1. The E_α-dependencies obtained for non-isothermal (open symbols) and isothermal (solid circles) epoxy cures.

5. Isoconversional method and consistency of isothermal and non-isothermal kinetics

The results of kinetic analyses of the isothermal and non-isothermal cures are intuitively expected to be consistent. However, they often found to be inconsistent. One of the major reasons of this disagreement is the prevalent use of the model-fitting methods. The latter tend to produce highly uncertain values of Arrhenius parameters that cannot be meaningfully compared with the isothermal values [2]. Because the model-free isoconversional methods are free of this uncertainty, they are likely to produce consistent kinetic results for the isothermal and non-isothermal data. To demonstrate this, we should first address the important issue of the application of the isoconversional method to the cure data obtained below the limiting glass transition temperature.

5.1. Analysis of incomplete cures

If cure is performed at a temperature above the limiting glass transition temperature, $T_{g,\infty}$ the system reaches full cure [10]. The latter is characterized by the maximum value of the heat release, Q_{rxn} which is independent of temperature. For this reason, the value of α determined as

$$\alpha = \frac{1}{Q_{rxn}} \int_0^t \frac{dQ}{dt}\, dt \tag{9}$$

can be called the absolute extent of cure.

The limiting value of the absolute extent of cure is independent of temperature and is equal to 1. When cured at a temperature below $T_{g,\infty}$, a system vitrifies before attaining full cure [10]. As a result, the heat flow from the curing system becomes practically undetectable at a certain value of the ultimate extent of cure, $\alpha_T < 1$. The cures performed at a temperature below $T_{g,\infty}$ can be called incomplete cures. The ultimate extent of incomplete cure can be estimated as

$$\alpha_T = \frac{Q_T}{Q_{rxn}} \tag{10}$$

where Q_T is the integrated heat release from a system cured at $T < T_{g,\infty}$. Unlike Q_{rxn}, the value of Q_T as well as of α_T decreases with decreasing the cure temperature.

Prime [11] mentions that the use of the relative extents of cure instead of the absolute values may affect kinetic evaluations. When using the isoconversional method, Salla and Ramis [12] have observed that the activation energies evaluated for the absolute and relative extents of cure are very close for the initial cure stages, but differ noticeably at higher extents of cure. Although the general feeling appears to be that the absolute extents of cure should be used for kinetic analyses, we intend to demonstrate that for incomplete cures the isoconversional methods yield the correct E_α-dependence providing the relative extents of cure are used instead of the absolute values.

According to Eq. (1), dQ/dt approaches zero when $f(\alpha)$ approaches zero. The typical models $(1-\alpha)^n$ and $\alpha^m(1-\alpha)^n$ assume that a system attains full cure, i.e. that α reaches 1. For incomplete cures, the value of α only reaches $\alpha_T < 1$. Inserting the value of α_T into the earlier models followed by their substitution into Eq. (1) would give rise to a constant non-zero heat flow after the practical cessation of cure that obviously contradicts to experimental observations. To be applicable to the incomplete cures, the reaction models should be taken in the form of Eqs. (11) and (12):

$$f(\alpha) = (\alpha_T - \alpha)^n \tag{11}$$

$$f(\alpha) = \alpha^m(\alpha_T - \alpha)^n \tag{12}$$

where α varies between 0 and α_T.

It is possible to derive analytical expressions for the activation energy, which one obtains by substituting into Eq. (5), the rate related to a fixed absolute value of α. Then, activation energy is

$$\begin{aligned} E_\alpha &\equiv -R\frac{d\ln(d\alpha/dt)_\alpha}{dT^{-1}} \\ &= -R\left[\frac{d\ln k(T)}{dT^{-1}}\right]_\alpha + \frac{RT^2}{f(\alpha)}\left[\frac{df(\alpha)}{dT}\right]_\alpha \end{aligned} \tag{13}$$

According to Eq. (5), the first term of the sum in Eq. (13) is the effective activation energy, E_α. Note that when the system approaches vitrification, the overall cure rate becomes diffusion controlled. The temperature dependence of the diffusion rate can be described by an Arrhenius equation, which yield an activation energy different from that of the chemically controlled process [13]. For cures, however, the rate of diffusion also depends on the extent of cure. This effect can be accounted for by introducing in Eq. (2) an additional term [14], which is omitted in 13 for the sake of simplicity.

The second term of the sum includes temperature derivative of the reaction model at a constant absolute extent of cure. With regard to Eqs. (11) and (12), this derivative is non-zero for incomplete cures because α_T varies with T. As a result, the second term of the sum in Eq. (13) differs from zero and, therefore, introduces a systematic error in the values of E_α. Because this term varies with α, it may also distort the actual shape of the E_α-dependence. The second term in Eq. (13) is always positive, which means that the respective E_α values should always be greater than the actual values of the activation energy. This deviation is expected to sharply increase at the extents of cure close to α_T when $f(\alpha)$ approaches zero (cf. Eqs. (11) and (12)) turning the second term of the sum in Eq. (13) into infinity.

The above-mentioned systematic error can be eliminated by replacing the absolute extents of cure with the relative values, α'. The latter can be obtained by dividing the absolute extents of cure, α for each temperature over the corresponding value of the ultimate extent of cure, α_T. Alternatively, the relative extent of cure, α' can be determined from DSC data as follows:

$$\alpha' = \frac{1}{Q_T}\int_0^t \frac{dQ}{dt}\,dt \tag{14}$$

The value of α' varies between 0 and 1. The cure rate also needs to be transformed in a similar fashion:

$$\frac{d\alpha'}{dt} = \frac{1}{\alpha_T}\frac{d\alpha}{dt} \equiv \frac{1}{Q_T}\frac{dQ}{dt} \tag{15}$$

The replacement of the absolute extents of cure with relative values, α' means that the values of the rate and time related to a fixed relative extent of cure should be respectively used in Eq. (13) to evaluate the activation energy. Additionally, the use of the relative extents of cure requires Eqs. (11) and (12) to be modified as follows:

$$f(\alpha') = (1-\alpha')^n \tag{16}$$

$$f(\alpha') = (\alpha')^m(1-\alpha')^n \tag{17}$$

If the relative extents of cure are used in Eq. (13), the temperature derivative of the reaction model at constant α' becomes zero. This means that the use of the relative extents of cure instead of the absolute values eliminates the systematic error in the value of the activation energy. Consequently, the isoconversional methods should yield the correct E_α-dependence, if one uses the relative extents of cure instead of the absolute values.

The theoretical conclusions can be illustrated by simulations. The equation of a first-order cure reaction (Eq. (16) with $n = 1$) has been substituted into the rate Eq. (2). The Arrhenius parameters have been chosen to be $A = 10^7\ \mathrm{min}^{-1}$, $E = 60\ \mathrm{kJ\ mol}^{-1}$. The cure kinetics have been simulated at the temperatures 60, 80, 100, and 120 °C, for which the ultimate extents of cure, α_T were taken to be 0.8, 0.85, 0.9, and 0.95, respectively.

The simulations allowed us to determine the rate values related to a fixed absolute extent cure. Substitution of these values into Eq. (18) (modification of Eq. (5)):

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT} \tag{18}$$

gives rise to the E_α-dependence presented in Fig. 2. The values of E_α show systematic deviations from the activation energy used for simulations. As was theoretically predicted, the use of the absolute extents of cure results in a positive systematic error in E_α that increases with increasing α and becomes most significant at α close to α_T (Fig. 2).

Substitution of the rate values related to the fixed relative extents of cure, α' into Eq. (18) results in the E_α values that are equal to the actual activation energy used in simulations (Fig. 2). Therefore, if the relative extents of cure are used for kinetics computations, the isoconversional method permits estimating the correct values of the activation energy for incomplete cures.

Our theoretical conclusions are based on the assumption that the kinetics of incomplete cures can be represented by the empirical equations (Eqs. (11) and (12)). Obviously, these equations do not describe

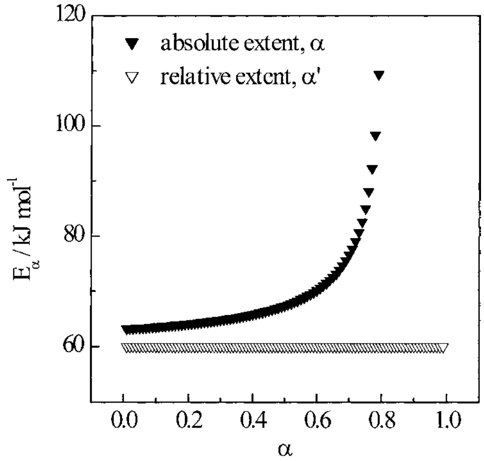

Fig. 2. The E_α-dependencies obtained for simulated isothermal data when using absolute (solid triangles) and relative (open triangles) extents of cure.

the process of vitrification. However, the occurrence of the systematic error in E_α is caused by the variation of α_T with T (cf. Eq. (13)) and, therefore, is independent of the particular form of the reaction model, $f(\alpha)$. Any non-empirical model, which is capable of adequately describing vitrification, should also be capable of describing the experimentally observed increase in α_T with T. Therefore, the use of such a model instead of Eqs. (16) and (17) should unavoidably predict a similar systematic error in E_α.

The previous conclusions can be tested by using an actual cure process that is "unaware" of theoretical assumptions. An ideal system for illustration purposes would obviously be a system that shows an activation energy, which does not vary with the extent of cure. Because we faced the difficulty of finding in the literature such a system, we used the epoxy-novolac system, which was under study in our laboratories. For this system, the absolute extents of cure, α_T were found (Eq. (10)) to be 0.75, 0.79, 0.84, 0.89, and 0.98 for respective temperatures 40, 60, 80, 100 and 120 °C. The relative extents of cure were evaluated by Eq. (14). In both cases, the converted data have been substituted into Eq. (18) to evaluate the E_α-dependencies. As seen in Fig. 3, the values of E_α determined from the absolute extents of cure are greater than the values estimated from the relative extents of cure. We can also see that the difference increases with the extent of cure and becomes most critical when α approaches α_T. Therefore, the behavior of the experimentally estimated E_α-dependencies is consistent with our theoretical predictions and simulations. Note that the obtained results explain the earlier observation by Salla and Ramis [12] who experimentally detected a similar difference in the respective E_α-dependencies including the sharp increase in E_α that is observed near α_T for the dependence evaluated from the absolute extents of cure. As follows from our theoretical analysis, this increase is a computational artifact.

5.2. E_α versus α for isothermal and non-isothermal data

Fig. 1 provides a comparison of the E_α-dependencies for the epoxy-anhydride cure that was performed under isothermal and non-isothermal conditions. As described in the previous section, we used the relative extents of cure for kinetic evaluations. The resulting E_α-dependence was rescaled by multiplying α' by $\overline{\alpha_T}$, which is an average α_T value for a series of isothermal experiments used for kinetic evaluations. As we can see (Fig. 1), the E_α-dependencies produced from isothermal and non-isothermal data are in excellent agreement.

Although the use of the model-free isoconversional method generally allows the agreement to be accomplished [1], differing E_α-dependencies may also be observed. The above-mentioned epoxy-novolac cure provides such an example. Fig. 4 shows the E_α-depen-

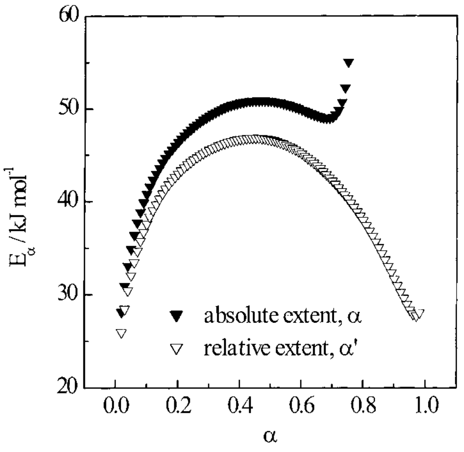

Fig. 3. The E_α-dependencies obtained for isothermal epoxy-novolac cure when using absolute (solid triangles) and relative (open triangles) extents of cure.

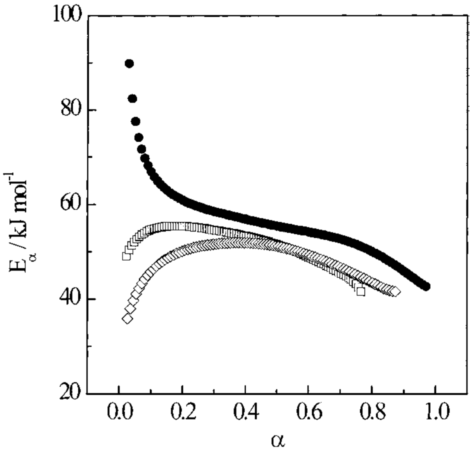

Fig. 4. The E_α-dependencies obtained for non-isothermal (solid circles) and isothermal (squares: $T = 40$, 60, 80 °C; diamonds: $T = 80$, 100, 120 °C) epoxy-novolac cures.

dencies obtained for isothermal and non-isothermal conditions. The Section 6 suggests an explanation to this effect.

6. Model-free analysis to unveil mass transfer effects

6.1. Effect of vitrification

If during the cure the glass transition temperature of a partially cured system exceeds the temperature of this system, the system vitrifies. The monomer molecules become frozen in their positions in the glassy state that results in the virtual cessation of polymerization. Stutz et al. [15] have studied the kinetics of epoxy-amine cure in the glass transition region and found that the process has very low activation energies (few kJ mol^{-1}). This means that vitrification should cause a decrease of the effective activation energy with increasing extent of reaction. The use of the model-free isoconversional methods allows one to observe this effect. For instance, we observed [14] this effect when curing the epoxy-amine system (Fig. 5). Temperature modulated DSC is capable of measuring the variation in the complex heat capacity as it changes during the cure. Vitrification causes a dramatic decrease in molecular mobility which is detected as a decrease in the complex heat capacity, C_p^* (Fig. 5).

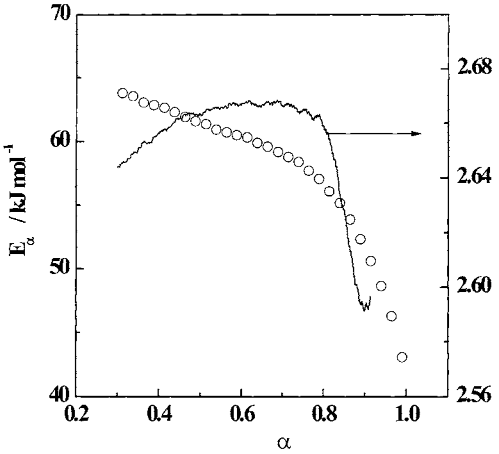

Fig. 5. Activation energy (open circles) and complex heat capacity (solid zig-zag line) for epoxy-amine cure. C_p^* has been measured at the following parameters: the heating rate 1 °C min^{-1}, the period 1 min, and the amplitude 1 °C.

6.1.1. Effect of viscosity on kinetics of initial cure stages

The reaction rate is generally determined by the rates of both chemical reaction and diffusion [16]. The ratio of the characteristic times of chemical reaction and diffusion determines which of these two processes is rate limiting. For epoxy cures, the change from chemical to diffusion control is usually associated with vitrification [11]. However, vitrification is not the only reason for diffusion control. The latter becomes operative if, for any reason, the characteristic time of relaxation of the reaction medium exceeds the characteristic time of a chemical reaction. According to Debye [17], the relaxation time for a molecule is directly proportional to viscosity:

$$\tau = \frac{4\pi a^3 \eta}{k_B T} \tag{19}$$

where η is the viscosity of the medium, a the molecular radius, and k_B is Boltzmann's constant. This suggests viscosity as a crucial factor of diffusion control.

Viscosities of epoxy curing systems demonstrate a complex temperature dependence, which is a superposition of two phenomena. Firstly, at a constant value of the molecular weight, viscosity decreases with increasing temperature. Eyring's theory of viscosity [18] gives rise to the Arrhenius type of temperature dependence:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \tag{20}$$

where E_η is the activation energy of the viscous flow, and η_0 is the pre-exponential factor. Eq. (20) usually holds for liquids well above their T_g. At temperatures closer to T_g, the temperature dependence of viscosity follows the WLF equation [19]. Secondly, an increase in the temperature accelerates the cure and, therefore, promotes an increase in both molecular weight and viscosity. This process ultimately results in vitrification at later cure stages. The diffusion control caused by vitrification has been extensively studied (see Prime [11] and references therein). Here, we consider the diffusion effect of viscosity on the isothermal and non-isothermal kinetics of the initial cure stages, when viscosity decreases with temperature. To our knowledge, this effect has not been addressed in the literature on epoxy cures.

The effective characteristic time of a process is the sum of the characteristic time of a chemical reaction and the characteristic time for reactants to diffuse in a viscous medium. By the law of the addition of kinetic resistances [16], the characteristic times can be replaced with the reciprocal rate constants:

$$k_{\mathrm{ef}}^{-1} = k^{-1} + k_{\mathrm{d}}^{-1} \tag{21}$$

where the subscripts "ef" and "d" denote the effective and diffusion rate constants, respectively. Because diffusion occurs as a succession of molecular jumps between the neighboring equilibrium positions, the characteristic time of the jump (k_{d}^{-1}) can be approximated by the relaxation time (Eq. (19)). The substitution of Eq. (20) into Eq. (19) allows one to derive the diffusion rate constant in the following form:

$$k_{\mathrm{d}} = C\exp\left(\ln T - \frac{E_\eta}{RT}\right) \tag{22}$$

where C is the pre-exponential factor. From Eq. (22), one can obtain the activation energy for diffusion, E_{d} as follows:

$$E_{\mathrm{d}} = -R\frac{\mathrm{d}\ln k_{\mathrm{d}}}{\mathrm{d}T^{-1}} = E_\eta + RT \tag{23}$$

If RT is much smaller than E_η, E_{d} is practically equal to E_η, which was experimentally found by several workers [18].

Substitution of the Arrhenius equation for k and Eq. (22) for k_{d} in Eq. (21) gives the effective activation energy:

$$E_{\mathrm{ef}} = -R\left(\frac{\mathrm{d}\ln k_{\mathrm{ef}}}{\mathrm{d}T^{-1}}\right) = \frac{(E_\eta + RT)k + Ek_\eta}{k + k_\eta} \tag{24}$$

where E is the activation energy of a chemical reaction. Epoxy cures are typically performed at moderate temperatures ($T < 200\,^{\circ}\mathrm{C}$) giving rise to the RT values less than 4 kJ mol^{-1}. If the E_η value is relatively big (70–90 kJ mol^{-1} [20,21]), RT in Eq. (24) can be safely neglected. Eq. (24) suggests that depending on the temperature, the effective activation energy may take values between E and E_η. Furthermore, the temperature behavior of E_{ef} should be different for the cures performed under isothermal and non-isothermal conditions. Because in an isothermal experiment the temperature is constant, E_{ef} has a constant value between E and E_η. This constant should, however, be different for isothermal experiments carried out in different temperature regions. In a non-isothermal experiment, temperature varies, causing E_{ef} to change with temperature. When using the isoconversional methods, this difference in the temperature dependencies should result in obtaining different E_α-dependencies for isothermal and non-isothermal data. To visualize this difference, we used Eq. (24) to simulate a first-order reaction whose kinetics is complicated by the temperature variation in viscosity:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_{\mathrm{ef}}(1-\alpha) \tag{25}$$

Although Eq. (25) does not represent the actual complexity of the cure kinetics, it is helpful to illustrate the previous theoretical conclusions. The individual values of kinetic parameters were taken to be $E = 50$ kJ mol^{-1}, $A = 8 \times 10^5$ min^{-1}, and $E_\eta = 80$ kJ mol^{-1}, $C = 10^{10}$ min^{-1}. The choice of the values for E and E_η was justified by the values reported in literature [11,20,21].

For non-isothermal conditions, Eq. (25) was integrated by using the Runge–Kutta method of fourth-order [22]. At each heating rate, we determined the temperatures, T_α that correspond to the extents of reaction $0.01 \le \alpha \le 0.5$ in intervals of 0.01. The upper limit of $\alpha = 0.5$ was chosen conventionally. In reality, the upper limit of α is determined by the extent of reaction, below which the temperature dependence of viscosity obeys Eq. (20). The obtained T_α values were inserted into Eq. (24) to plot the effective activation energy, E_α as a function of the temperature and the corresponding extent of reaction. The resulting surface plot of E_α is shown in Fig. 6. Isothermal surface plot was performed, spanning the temperature range of non-isothermal simulations. The value of the temperature was substituted into Eq. (24), and the value of α was varied in the range 0.01–0.5 in intervals of 0.01. The results are shown in Fig. 7.

Although both surface plots show a decrease in E_α from ~75 to ~60 kJ mol^{-1} with increasing temperature, the shapes of the plots are obviously different (Figs. 7 and 8). These plots allow for predicting the shapes of E_α-dependencies that should result from applying the isoconversional method to isothermal and non-isothermal data. In order to do that, we have

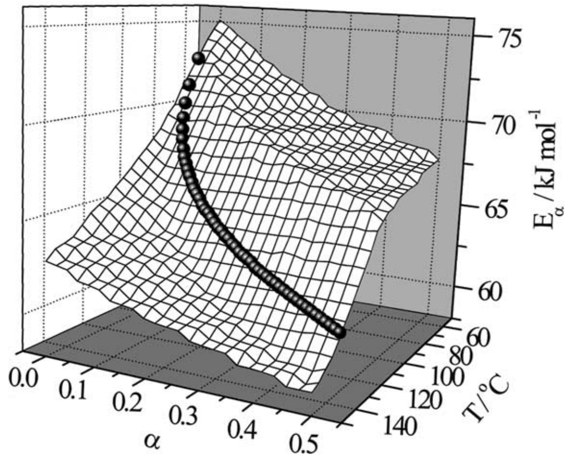

Fig. 6. Surface plot of activation energy as a function of extent of reaction and temperature for simulated data under non-isothermal conditions. Spheres represent the α–T path for the heating rate of 5 °C min^{-1}.

to cut the surface along the α–T path taken by the reaction system. A projection of such cuts on the α–E_α plane gives the shape of the E_α-dependencies. Then, in a non-isothermal experiment we should observe an E_α-dependence that decreases from E_η to E with increasing α. Isothermal experiments should yield a constant E_α, the absolute value of which decreases when the temperature region of experiments is moved to higher temperatures.

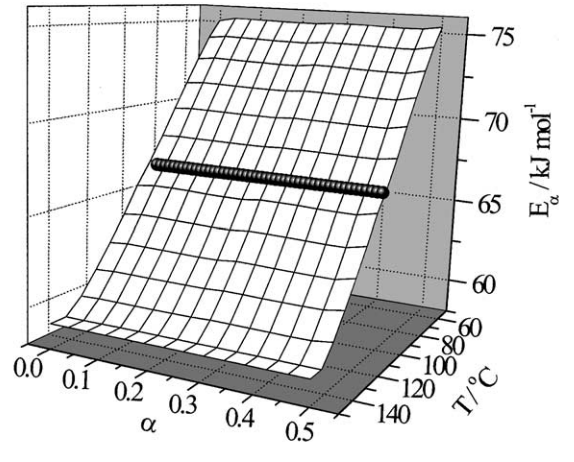

Fig. 7. Surface plot of activation energy as a function of extent of reaction and temperature for simulated data under isothermal conditions. Spheres represent the α–T path for the temperature of 100 °C.

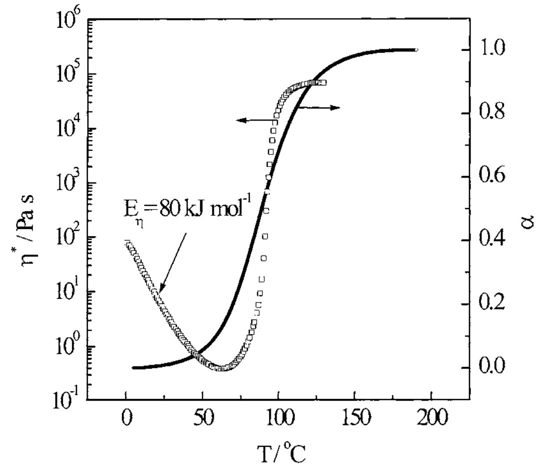

Fig. 8. Experimentally measured temperature dependencies of the extent of cure and dynamic viscosity for the epoxy system cured at the heating rate of 2 °C min^{-1}. Viscosity measurements have been carried out on a parallel plate setup (Paar Physica) at frequency 1 Hz.

Therefore, if the difference in the E_α-dependencies for the epoxy-novolac system (Fig. 4) is actually caused by the viscous relaxation, the activation energy for the initial cure stage should be close to the activation energy of the viscous flow. Indeed, the initial stage of the non-isothermal cure is accompanied by a significant decrease in viscosity (Fig. 8) that is accurately described by Eq. (20) with $E_\eta = 80$ kJ mol^{-1}, which is very close to the activation energy determined for the initial stage of the non-isothermal cure (Fig. 4). It is also in agreement with the theoretical predictions that the non-isothermal data give rise to a decreasing E_α-dependence. Unlike the simulated data, the actual isothermal data do not yield a constant value of E_α, because the chemical stage of cure usually involves several elementary steps. To observe the predicted for isothermal data decrease in the absolute values of E_α with increasing temperature, we have evaluated the E_α-dependencies using two data sets corresponding to the following temperatures: 40, 60, 80 °C and 80, 100, 120 °C. The average temperature for these two sets of data differs by 40 °C. As was theoretically predicted (Fig. 7), the experiments performed at a greater average temperature yield smaller absolute values of E_α for the initial cure stage (Fig. 4).

7. Conclusion

The isoconversional method has been applied to the sets epoxy cure data obtained under isothermal and non-isothermal conditions. The method permits obtaining consistent kinetic results in the form of similar E_α-dependencies derived from isothermal and non-isothermal data. Analysis of such dependencies also allows for untangling complex cure processes that may include different chemical reactions or a chemical reaction complicated by a mass transfer processes such as viscous relaxation and vitrification.

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