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Mechanistic modeling of the epoxy–amine reaction
Model derivations

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Abstract

A series of kinetic models of the epoxy–amine addition have been derived based on the assumption that its rate-determining step overcomes the formation of an intermediate equilibrium epoxy–hydroxyl complex. The model fundamentals and the main approximations have been discussed. An alternative mechanistic description within the classical scheme has been also presented. In spite of the ability of the last to describe the experiments almost perfectly, it has been considered that more reliable model predictions will have been obtained by following the intermediate equilibrium complex schemes.

Keywords: Differential scanning calorimetry; Reaction kinetics; Epoxy–amine reaction; Mechanistic models

1. Introduction

One of the most practically important reactions in the field of thermoset processing is the epoxy–amine addition. It proceeds due to the opening of oxirane rings of the epoxy component by hydrogen atoms of the amine component thus joining the last in copolymer chains.

In terms of reacting groups, the epoxy–amine addition kinetics is based on the below given generally accepted consecutive reaction scheme [1–7], e.g. in Scheme 1, where A_p and A_s express the primary and secondary amine hydrogen atoms, E and A_t denote the epoxy and tertiary amine groups; OH and E…OH represent all currently existing hydroxyl groups and those involved in intermediate complexes, respectively; k_i and k'_i ($i = 1, 2$) are Arrhenius-type rate constants.

Horie et al. [8] have proposed the above scheme after findings from other authors [9,10] who experimentally established that the epoxy–amine reaction was markedly accelerated in the presence of hydroxyl containing substances. Since the hydroxyl groups are one of the reaction products then the reaction can be considered to be autocatalytic.

The autocatalytic kinetics of the epoxy–amine addition is mathematically described using the following system of velocity ordinary differential equations (ODE) [4–8,11–21]:

$$-\frac{da_1}{dt} = 2k_1[b + (e_0 - e)]ea_1 \tag{1a}$$

$$-\frac{da_2}{dt} = k_1[b + (e_0 - e)]e(ra_2 - a_1) \tag{1b}$$

$$-\frac{de}{dt} = k_1[b + (e_0 - e)]e(a_1 + ra_2) \tag{1c}$$

where e and e_0 are the current and initial concentrations of epoxy groups, a_1 and a_2 the concentrations of primary and secondary amine hydrogen atoms, respectively, $r = k_2/k_1 = k'_2/k'_1$ their reactivity ratio and b is a parameter involving the ratio of the non-catalytic rate constant over the autocatalytic one; its exact meaning differs depending of the accepted initiation path.

We have to emphasize, that the formalism applied to express the concentration of the amine component can lead to somewhat different both velocity and mass balance equations

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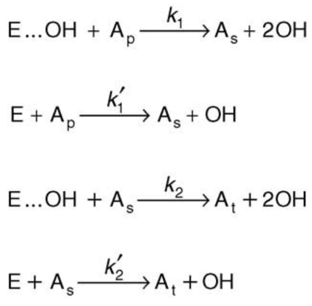


Scheme 1.

[18–21]. The definition of r can also differ. According to the amine hydrogen principle, the ideal value of r defines equally reactive primary and secondary amine hydrogen atoms, i.e. $r = 1$ (or $k_1 = k_2$ and $k'_1 = k'_2$). Conversely, the amine group formalism supposes a twice more reactive primary amine group (having two possibilities to react) compared to the secondary one (having one possibility to react), i.e. $r = 1/2$ (or $k_1 = 2k_2$ and $k'_1 = 2k'_2$). As the notation below Eq. (1) shows, we accept the amine hydrogen mass balance principle.

The effect of reactivity ratio is known in literature as kinetic substitution effect (KSE). It is one of the mostly debatable problems in the field of epoxy–amine reaction but negative KSE or less reactive secondary amines, is often considered to be a more probable phenomenon [4–6,16]. A detailed analysis of KSE was given by Miller and Macosko [22], Rozenberg [4] and more recently, by Mijovic et al. [16] and Matejka [23].

Eq. (1) imply that the autocatalytic reaction has to be promoted; otherwise, it will never start. The initiation term was sometimes observed to be a temperature-independent parameter. In these cases, it has been ascribed to the initial hydroxyl content being always a product of synthesis even in very low molecular epoxies [4,12,13,18,24–28], i.e. $b = k'_1/k_1[\mathrm{OH}]_0 = k'_2/k_2[\mathrm{OH}]_0$, where $k'_1/k_1 = k'_2/k_2 \approx 1$. In other cases, b was found to vary with temperature indicating a competitive bimolecular initiation [2–8,29–36], i.e. $b = k'_1/k_1 + [\mathrm{OH}]_0 = k'_2/k_2 + [\mathrm{OH}]_0$, where $k'_1/k_1 = k'_2/k_2 \ll 1$.

The derivation of Eq. (1) is based on several approximations. The first one considers that the volume change during the reaction advance does not influence dramatically the kinetics. Its effect has been recently discussed in some detail [6] but it seems to be important if the initial molar amine to epoxy ratio, R_0, is varied significantly.

The second approximation postulates that the reaction rates depend on the concentrations of reacting groups rather than those of all individual species—monomers, dimers, trimers, etc. This assumption has been proved to be valid well above the theoretical gel point, where the molecular motion might be restricted. In spite of this, the kinetics was not observed to be altered above the gel point. Even more, it sometimes seemed accelerated within a part of this range [35].

The definition of b and r illustrates the third approximation accepted in Eq. (1), namely each initiation rate constant is proportional to the corresponding autocatalytic one. As is shown later, the last two approximations will have been accepted to develop the mechanistic models of the epoxy–amine addition, although the third one appears to be reasonable for very low molecular epoxy formulations, where $b \ll 1$. The effect of the volume change will not be discussed further in this study.

Applying the well known normalizations, viz., $e/e_0 = (1 - \alpha)$, $[\mathrm{OH}]/e_0 = \{[\mathrm{OH}]_0 + (e_0 - e)\}/e_0 = c_0 + \alpha$, $a_1/e_0 = \lambda_1$ and $a_2/e_0 = \lambda_2$, the following set of dimension-free ODE is obtained:

$$-\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = 2K_1(B + \alpha)(1 - \alpha)\lambda_1 \qquad (2a)$$

$$-\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = K_1(B + \alpha)(1 - \alpha)(r\lambda_2 - \lambda_1) \qquad (2b)$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1(B + \alpha)(1 - \alpha)(\lambda_1 + r\lambda_2) \qquad (2c)$$

where α is the so-called degree of epoxy conversion λ_1 and λ_2 the normalized concentrations of the primary and secondary amine hydrogen atoms, respectively, $K_1 = k_1 e_0^2$ and $K'_1 = k'_1 e_0$ the dimension-free rate constants and B includes the ratio of the non-catalytic rate constant over the autocatalytic one, i.e. its expression again depends on the accepted initiation pathway.

The degree of epoxy conversion can be measured using different physical–chemical methods–analysis of reactive groups [4,23,37], chromatography [12,18,24,25], conductivity and dielectric measurements [33,38–41], T_g-monitoring [14,26–28], FTIR [32–36,42–48], DSC [2,3,7,29–32,49–60], as well as some specially designed techniques [61–63]. In our opinion, DSC and FTIR appear to be the most important conventional techniques. DSC allows to perform the kinetic analysis in isothermal and programmed temperature modes, as well as to combine the isothermal and non-isothermal kinetics [3,7,30,49–60]. FTIR in the near infrared region permits to obtain both α and λ_1, whereas λ_2 can be determined from the mass balance equations [20,34–36]. The reactivity ratio can be also determined using near-FTIR spectroscopy at the maximum of λ_2 curves, where $\mathrm{d}\lambda_2/\mathrm{d}t = 0$, $\alpha = 0.5$ and $r = k_2/k_1 = \lambda_1/\lambda_2$ [34].

If the reactivity of primary and secondary amine hydrogen atoms is equal, i.e. $r = 1$ (or $k_1 = k_2$ and $k'_1 = k'_2$), then Eq. (2) transform into the overall model of Horie et al. so-called [29–33], viz.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1(B + \alpha)(1 - \alpha)(R_0 - \alpha)$$
$$= (K'_1 + K_1\alpha)(1 - \alpha)(R_0 - \alpha) \qquad (3)$$

The overall velocity equation describing the reaction of stoichiometric compositions or $R_0 = 1$, becomes:

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha)(1-\alpha)^2 = K_1(B+\alpha)(1-\alpha)^2 \quad (4)$$

The overall rate constants of some epoxy–amine reactions have been determined mainly in equimolar quantities of the components as the slope and intercept of the plot [8]:

$$\dot{r} = \frac{d\alpha}{dt}\frac{1}{(1-\alpha)^2} = K_1' + K_1\alpha \quad (4')$$

where $\dot{r}$ is a typical expression in the autocatalytic kinetics known as reduced reaction rate.

The analysis of literature shows that experiments sometimes obeyed Eq. (4), at least in limited ranges of conversion and temperature [2,13,17,24–28,33], but deviations from the overall model have been more often established [3,4,8,14–16,18–21,43–63]. To obtain the values of the overall rate constants in these cases, Kamal et al. have proposed the following model of the epoxy–amine reaction [64]:

$$\frac{d\alpha}{dt} = K_1(B+\alpha^m)(1-\alpha)^n = (K_1' + K_1\alpha^m)(1-\alpha)^n \quad (5)$$

where m and n are experimentally adjustable parameters.

This widely used formal velocity equation is more or less acceptable to study the kinetics if $R_0 = 1$, but it is completely unclear if $R_0 \neq 1$. As is shown by Vyazovkin and Sbirrazzuoli [65], the model-free analysis is a preferable technique to study the formal kinetics [66,67]. These authors also pointed out that some mechanistic details can be discovered applying their approach. On the other hand, the Kamal's model might have some usefulness, as is commented below.

We recently studied an epoxy–amine reaction following the formal equation of the form $d\alpha/dt = K_1(B+\alpha)(1-\alpha)^n$ and an extended reactivity ratio model [21,53]. It has been shown that positive deviations from the overall model (or $n < 2$ in terms of the Kamal's model [53]), yielded a positive KSE (or $r > 1$ in the terms of Eq. (2) [21]). At the same time, the best fit values of the parameters K_1 and B according to the formal model were found exactly the same as those at the beginning of reaction according to the mechanistic ones.

The above finding has been theoretically proved in the recent study of Talbot [68]. The author of this noteworthy work has also shown that the transform of classical into Kamal's model is possible but at certain restriction with respect to the power exponents, namely n may vary as a rule within 1 and 2, whereas m should typically lie between 0.67 and 1.

Recent results on the kinetics of different epoxy–amine reactions performed using near-FTIR indicated a higher reactivity of primary amine hydrogen atoms, i.e. $r < 1$ (negative KSE) [34,36], but positive deviations from Eq. (4) [35]. There are several studies found in literature attempting to explain the mentioned disagreement.

Using a semi-empirical model Paz-Abuin et al. [35] have postulated that the auto-acceleration phenomenon in epoxy systems is similar to that observed in vinyl ester resins. The parameter in their model has been assigned to the-free volume contraction and to an increase of local concentration of reacting species.

Rozenberg [4], Mijovic et al. [16] and Xu et al. [17] have assumed the formation of different transition state complexes but the model of Mijovic et al. led to forth order mechanism, whereas Xu et al. did not succeed to distinguish between the different mechanisms, as they commented.

Flammersheim [49] and Riccardi et al. [51] have accepted the formation of an equilibrium epoxy–hydroxyl complex resulting in pseudo-second-order rate expressions and postulated the main objectives of this mechanistic scheme. It has been further developed by Flammersheim [50] and Swier and Van Mele [57] who pointed out that other complexes were also possible to exist. Although this approach seems physically sound, the high number of adjustable parameters makes their analysis debatable, as Flammersheim pointed out.

In this study, we have attempted to derive a mechanistic model of the epoxy–amine addition elaborating an extended amine reactivity scheme, we have proposed recently [21], into the model of Flammersheim and Riccardi et al. This is one of the objectives of the study. The second aim of this work is to present exact mathematical descriptions of the multiple equilibrium schemes similar to that proposed by Swier and Van Mele.

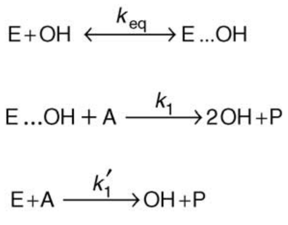
2. Model development

2.1. Average amine reactivity models

Flammersheim [49,50] and Riccardi et al. [51] have tried to explain the deviations from the model of Horie et al., as well as to couple the isothermal and non-isothermal data. They have proposed the scheme of the epoxy–amine reaction, e.g. in Scheme 2, where A and P express the primary or secondary amine reactant and secondary or tertiary amine product, respectively, E...OH the equilibrium epoxy–hydroxyl complexes formed and K_{eq} is an equilibrium constant.

The physical–chemical picture, which follows from Scheme 2, can be clearly depicted in terms of the theory of activated complex.

The equilibrium constant defines the existence of E and OH groups in E...OH covalent bond complexes together



Scheme 2.

with free E and OH groups. Both E...OH and free E groups attempt to form transition state complexes, E...OH...A and E...A, respectively. Each of them may decompose either to products or to reactants and the rate constants k_1 and k'_1 define the decomposition rates of both transition state complexes into identical products.

This mechanistic scheme has been mathematically described using an equilibrium constant expression and an overall velocity equation [51], viz.

$$K_{\mathrm{eq}} = \frac{[\mathrm{E}\ldots\mathrm{OH}]}{[\mathrm{E}][\mathrm{OH}]} \tag{6a}$$

$$-\frac{\mathrm{d}e}{\mathrm{d}t} = k_1[\mathrm{E}\ldots\mathrm{OH}]a + k'_1[\mathrm{E}]a \tag{6b}$$

After the replacement of Eq. (6a) into Eq. (6b), one can convert the last into another form describing the reaction kinetics in terms of number of species participating in the transition state complexes, viz.

$$-\frac{\mathrm{d}e}{\mathrm{d}t} = k_1K_{\mathrm{eq}}[\mathrm{OH}][\mathrm{E}]a + k'_1[\mathrm{E}]a = k_{\mathrm{ef}}([\mathrm{OH}] + b)[\mathrm{E}]a \tag{6c}$$

where all symbols in square brackets denote molar concentrations, a the current concentration of all amine hydrogen atoms, $k_{\mathrm{ef}} = k_1K_{\mathrm{eq}}$ an effective autocatalitic rate constant and $b = k'_1/k_1K_{\mathrm{eq}}$ is the ratio of the non-catalytic rate constant over the effective autocatalytic one.

The solution of Eq. (6) requires additionally the mass balance equations that arise from the equilibrium constant relation, viz.

$$e = [\mathrm{E}] + [\mathrm{E}\ldots\mathrm{OH}]$$

$$[\mathrm{OH}]_0 + e_0 - e = [\mathrm{OH}]_0 + [\mathrm{OH}] + [\mathrm{E}\ldots\mathrm{OH}]$$

where the terms at left represent the current concentrations of all epoxy and hydroxyl groups, respectively.

As one can establish, the two competitive reactions alter in different manner the equilibrium. The autocatalytic reaction turns it right or [E] and [OH] decrease. Conversely, the non-catalytic reaction turns the equilibrium left and, as a result, [E] and [OH] increase. On the other hand, Eq. (6) predit the boundary cases similarly to the model of Horie et al.:

- If $K_{\mathrm{eq}} \gg 1$, then all E and OH groups exist in state of E...OH complexes and, in turn, the reaction becomes autocatalytic. In fact, it is bimolecular but it behaves as three molecular since [OH] continuously increases.
- If $K_{\mathrm{eq}} \ll 1$, then all epoxy groups are in the free state and the main reaction becomes entirely non-catalytic.

The normalized dimension free form of Eq. (6) in stoichiometric ratios of the component has been derived previously [51]:

$$K^* = \frac{y}{(c_0 + \alpha - y)(1 - \alpha - y)} \tag{7a}$$

$$\begin{aligned} -\frac{\mathrm{d}\alpha}{\mathrm{d}t} &= K'_1(1 - \alpha - y)(1 - \alpha) + K_1y(1 - \alpha) \\ &= K_1[B'(1 - \alpha - y) + y](1 - \alpha) \end{aligned} \tag{7b}$$

or after the replacement of Eq. (7a) into Eq. (7b), one can obtain:

$$\begin{aligned} -\frac{\mathrm{d}\alpha}{\mathrm{d}t} &= K'_1(1 - \alpha - y)(1 - \alpha) \\ &\quad + K_{\mathrm{ef}}(c_0 + \alpha - y)(1 - \alpha - y)(1 - \alpha) \end{aligned} \tag{7c}$$

where $y = [\mathrm{E}\ldots\mathrm{OH}]/e_0$ is the normalized concentration of epoxy groups involved in E...OH complex formation, $K_1 = k_1e_0$, $K_{\mathrm{ef}} = k_{1,\mathrm{ef}}\,e_0^2$ and $K'_1 = k'_1e_0$ the normalized rate constants, $K^* = K_{\mathrm{eq}}e_0$ the dimensionless equilibrium constant and B' is the ratio of the non-catalytic rate constant over the bimolecular autocatalytic one.

Comparatively to the overall model of Horie et al., Eq. (4), the pseudo-bimolecular scheme of Flammersheim–Riccardi is represented by Eq. (7). This scheme has been rejected for the reaction of phenyl glycidyl ether with *N*-methyl benzyl amine in the early work of Xu et al. [17], but it seemed to be valid in many cases including those when other model systems were studied [45–47,57–60].

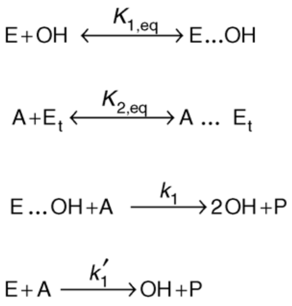
The second form of the model of Flammersheim–Riccardi, Eqs. (6c) and (7c), shows its principal difference from the model of Horie et al. The variables [E] and [OH] in the former express the molar concentrations of E and OH groups which are not involved in the formation of bimolecular E...OH complexes. On the contrary, those in the classical model of Horie et al. express their total quantities, i.e. $[\mathrm{E}]_{\mathrm{t}} = e$ and $[\mathrm{OH}]_{\mathrm{t}} = [\mathrm{OH}]_0 + (e_0 - e)$. The mentioned advantage of Eqs. (6c) and (7c) is commented in the next subsection (Section 2.2).

2.2. *Multiple equilibrium and average amine reactivity models*

Several authors have recently proposed that more than one covalent bonds can be formed in the reactive mixture [4,17,50,57–60]. As Swier and Van Mele have pointed out, there might be either reactive or non-reactive equilibrium complexes. While the former facilitate the reaction by transferring into activated complexes causing accelerated rate, the non-reactive complexes reduce the concentration of reacted species and, in turn, retard the reaction. However, the mathematical description of such an assumption is not so simple.

For example, some multiple equilibrium models similar to those proposed recently [50,57] can be considered within the overall amine reactivity model of Flammersheim and Riccardi et al. on the basis of Schemes 3 and 4.

Scheme 3 representing simultaneously existing epoxy–hydroxyl (E...OH) and amine–ether link ($\mathrm{A}\ldots\mathrm{E}_{\mathrm{t}}$) complexes can be described in equimolar proportion of the components



Scheme 3.

using the following set of dimension-free ODE:

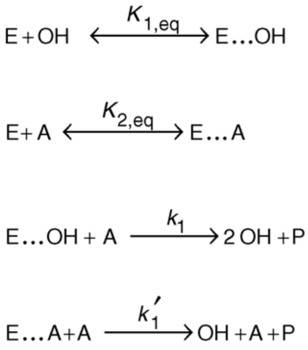
$$K_1^* = \frac{y}{(c_0 + \alpha - y)(1 - \alpha - y)} \tag{8a}$$

$$K_2^* = \frac{z}{(p - z)(1 - \alpha - z)} \tag{8b}$$

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1'(1 - \alpha - y)(1 - \alpha - z) + K_1 y(1 - \alpha - z) \tag{8c}$$

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1'\underset{[E]_{fr}/e_0}{(1-\alpha-y)}\underset{[A]_{fr}/a_0}{(1-\alpha-z)} + K_1K_1^*\underset{[OH]_{fr}/e_0}{(c_0+\alpha-y)}\underset{[E]_{fr}/e_0}{(1-\alpha-y)}\underset{[A]_{fr}/a_0}{(1-\alpha-z)} \tag{8d}$$

where y and z are normalized concentrations of the epoxy groups and amine hydrogens which are involved in E. . .OH and A. . .E$_t$ complexes, respectively, p the initial normalized concentration of ether groups that is close to unity for low molecular equimolar systems, i.e. $p = 1 + c_0$; $K_1^* = K_{1,\mathrm{eq}}e_0$ and $K_2^* = K_{2,\mathrm{eq}}e_0$ form a couple of dimensionless equilibrium constants defined by the above relations; the normalized concentrations of the free functionalities are notated below the velocity equation.



Scheme 4.

The multiple equilibrium Scheme 4 depicting two simultaneously existing intermediate reactive complexes, respectively, epoxy–hydroxyl (E. . .OH) and epoxy–amine (E. . .A), can be again described following the approach of Flammersheim and Riccardi et al., viz.

$$K_1^* = \frac{y}{(c_0 + \alpha - y)(1 - \alpha - y - u)} \tag{9a}$$

$$K_2^* = \frac{u}{(1 - \alpha - u)(1 - \alpha - y - u)} \tag{9b}$$

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1'(1 - \alpha - u)u + K_1(1 - \alpha - u)y \tag{9c}$$

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1'K_2^*\underset{[E]_{fr}/e_0}{(1-\alpha-y-u)}\underset{[A]_{fr}/e_0}{(1-\alpha-u)^2} + K_1K_1^*\underset{[OH]_{fr}/e_0}{(c_0+\alpha-y)}\underset{[E]_{fr}/e_0}{(1-\alpha-y-u)}\underset{[A]_{fr}/e_0}{(1-\alpha-u)} \tag{9d}$$

where y, u and $y+u$ are normalized concentrations of hydroxyl groups, amine hydrogen atoms and epoxy groups involved in E. . .OH and E. . .A complexes, correspondingly, and K_1^* and K_2^* denote another couple of equilibrium constants.

The second form of the model of Flammersheim–Riccardi, Eqs. (8d) and (9d), expresses the well-known schemes of the epoxy–amine reaction proposed within the classical model of Horie et al. [8], but adapted in terms of the model of Flammersheim–Riccardi [49,51].

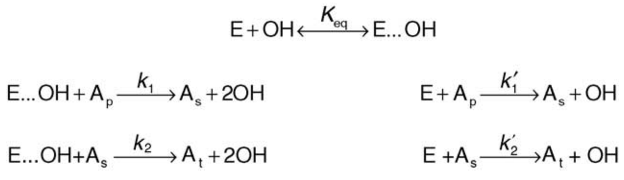
Eq. (8d) can be obtained by replacing the variable y from Eq. (8a) into Eq. (8c). It represents Scheme 2 but in case of the formation of E. . .OH and A. . .E$_t$ complexes. On the contrary, Eq. (9d) describes another possible scheme of the epoxy–amine addition discussed in the studies of Rozenberg and Xu et al. [4,17]. It reflects the kinetics of two competitive catalytic reactions but taking place in the presence of simultaneously existing E. . .A and E. . .OH complexes.

As is evident from the second form of the model of Flammersheim–Riccardi, Eqs. (8d) and (9d) describe the epoxy–amine kinetics in terms of number of molecules participating in the transition state complexes, in contrast to Eqs. (8c) and (9c) which express it in terms of reaction order. At the same time, the second form of the model of Flammersheim–Riccardi shows the basically accepted schemes of the reaction studied.

A similar definition of the effective rate constants according to Eqs. (8) and (9) has been formulated in the recent studies of Vinnik and Roznyatovski [69,70], besides of some debatable points in their approach.

The analysis of the above sets of ODE confirms the statement of Swier and Van Mele who pointed out that the reactive complexes (E. . .OH and E. . .A) accelerate the reaction. According to these models the autocatalytic reaction has to be accelerated since the effective rate-constants increase. It is also seen that the non-reactive complexes (A. . .E$_t$) retard the reaction due to the decrease of free hydrogen atoms when the reaction progresses.

Eqs. (8) and (9) indicate that each equilibrium relation introduces an additional variable. According to Eqs. (9a) and (9b) the variables might be correlated in some cases.



Scheme 5.

2.3. Reactivity ratio models

If the reactivity of the amine hydrogen atoms is different, then the epoxy–amine reaction can be represented using combination of the Schemes 1 and 2 in Scheme 5.

Consequently, the reactivity ratio model according to Flammersheim and Riccardi et al. can be expanded into the following set of velocity ODE:

$$K^* = \frac{y}{(1-\alpha-y)(c_0+\alpha-y)} \tag{10a}$$

$$-\frac{d\lambda_1}{dt} = 2K_1[B'(1-\alpha-y)+y]\lambda_1 \tag{10b}$$

$$-\frac{d\lambda_2}{dt} = K_1[B'(1-\alpha-y)+y](r\lambda_2-\lambda_1) \tag{10c}$$

$$\frac{d\alpha}{dt} = K_1[B'(1-\alpha-y)+y](\lambda_1+r\lambda_2) \tag{10d}$$

A similar model of the epoxy–amine reaction has been recently applied by Swier and Van Mele to study far more complicated reaction schemes [57]. Their model has been tested on some typical epoxy systems as well as in reaction induced phase separating formulations and it well described the reaction advance of the systems they studied [58–60]. Swier and Van Mele have first implemented the model of Flammersheim–Riccardi into the four rate-constant schemes but in our opinion, their approach requires additional theoretical considerations as those presented in one of subsections that follow.

As one can see, to obtain the analytical form of Eq. (10), it is necessary to accept the same approximations as those applied in the solution of the classical autocatalytic model, namely:

- The rate constants k_1 and k_2 and the equilibrium relation K_{eq} express the velocity equations in terms of reacting groups.
- The ratios r and b are expressed as $r = k_2/k_1 = k'_2/k'_1$ and $b = k'_1/k_1 = k'_2/k_2$ by definition.

The secondary amine rate expressions might be excluded from Eqs. (2) and (10), since λ_2 can be determined from the mass balance equations. In stoichiometric proportions of the reaction components $\lambda_2 = 1 - \alpha - \lambda_1$ and the KSE model according to Horie et al., Eq. (2), are reduced to:

$$-\frac{d\lambda_1}{dt} = 2K_1(B+\alpha)(1-\alpha)\lambda_1 \tag{11a}$$

$$\frac{d\alpha}{dt} = K_1(B+\alpha)(1-\alpha)[\lambda_1(1-r)+r(1-\alpha)] \tag{11b}$$

The corresponding simplified form of Eq. (11) in terms of the model of Flammersheim and Riccardi et al. transforms to:

$$K^* = \frac{y}{(1-\alpha-y)(c_0+\alpha-y)} \tag{12a}$$

$$-\frac{d\lambda_1}{dt} = 2K_1[B'(1-\alpha-y)+y]\lambda_1 \tag{12b}$$

$$\frac{d\alpha}{dt} = K_1[B'(1-\alpha-y)+y][\lambda_1(1-r)+r(1-\alpha)] \tag{12c}$$

It is noteworthy that the dependence of α versus λ_1 derived following Eq. (12) is the same as that extracted from Eq. (11), viz.

$$\alpha = 1 - \frac{[\lambda_1(1-r)+\lambda_1^{r/2}]}{2-r} \tag{13}$$

Consequently, Eq. (13) becomes a test dependance in the epoxy–amine addition kinetics. If one will have reliable data for α and λ_1, e.g. obtained using FTIR, the plot of r versus α can be easily constructed in the whole conversion range. If the experimental data obey Eq. (13) and Horie plot exhibits the opposite trend, then the model of Flammersheim–Riccardi extended by us seems to be, at least, highly probable.

As one can establish, the classical scheme of Horie et al., Scheme 1 and its modification proposed within the model of Flammersheim and Riccardi et al., Scheme 5, result in different mathematical descriptions–Eqs. (11) and (12). The earlier studies of the former have been reviewed by several authors [4,16,22,23]. Unfortunately, their systematic did not appear exact in all cases since the model of Horie et al. has been derived following different mass balance formalisms. As is mentioned, the amine component expression yielded different velocity and mass balance equations. A more detail discussion on the reactivity ratio formalism can be found in literature [21,53].

2.4. Extended reactivity ratio models

To explain why a good description of the experiment cannot be obtained by using Eq. (11), we have recently attempted to extend it in terms of the classical Scheme 1 [21]. This modified kinetic model is based on the assumption that the amine monomer is less reactive than all primary amine ended adducts. In other words, we have modified the well-known scheme of the amine hydrogen reactivity proposed by Dusek et al. [37] into the scheme presented in Fig. 1.

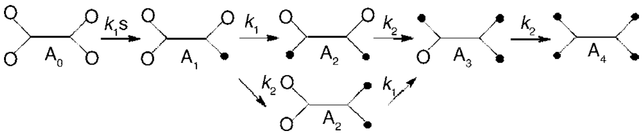


Fig. 1. Schematic representation of the amine hydrogen reactivity according to the modified reactivity ratio model [21].

Similarly to the original notification of Dusek et al., the unfilled circles in Fig. 1 mean the non-reacted hydrogens, whereas the filled circles express the reacted ones. According to the scheme, it has been suggested that the solubility of primary amine ended adducts–either in the pure epoxy or between themselves–is favored by stronger interactions in comparison to those of the pure amine monomer. Note that due to the hydrogen bonding most of the amine hardeners rapidly tend to crystallize from the monomer mixture. The weaker interactions in the last have been accounted by a semi-empirical parameter s supposed to be typically less than unity. Based on this assumption we have obtained the following set of dimension-free velocity ODE [21]:

$$-\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = 4K_1 s(B+\alpha)(1-\alpha)\lambda_0 \tag{14a}$$

$$-\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = 2K_1(B+\alpha)(1-\alpha)[\lambda_1 - \lambda_0(1-s)] \tag{14b}$$

$$-\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = K_1(B+\alpha)(1-\alpha)[r\lambda_2 - \lambda_1 + \lambda_0(1-s)] \tag{14c}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1(B+\alpha)(1-\alpha)[\lambda_1 - \lambda_0(1-s) + r\lambda_2] \tag{14d}$$

where λ_0 is the normalized concentration of the amine monomer.

We have to emphasize that some results found in literature appear to confirm the above-presented scheme. For example, Jones et al. have studied some model epoxy–amine reactions using a versatile technique consisting of radioactive labeling of the amine component, HPLC with radioactive detection and computer simulations [61–63]. The reaction of phenyl glycidyl ether with *m*-phenylene diamine has been described using a four rate-constant model, i.e. they did not succeed to resolve the A_2 and A'_2 products. In spite of this, the analysis of their rate-constant values seems to indicate $r < 1$, but $s < 1$, as well.

Accepting all the above-mentioned approximations, one can introduce another function of the amine reactivity, such as that proposed in the derivation of Eq. (14) and to modify the model of Flammersheim–Riccardi. Having in mind that different amine functionalities do not affect the E· · ·OH equilibrium, the following expanded model of the epoxy–amine addition is thus derived:

$$K^* = \frac{y}{(1-\alpha-y)(c_0+\alpha-y)} \tag{15a}$$

$$-\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = 4K_1 s[B'(1-\alpha-y)+y]\lambda_0 \tag{15b}$$

$$-\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = 2K_1[B'(1-\alpha-y)+y][\lambda_1 - \lambda_0(1-s)] \tag{15c}$$

$$-\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = K_1[B'(1-\alpha-y)+y][r\lambda_2 - \lambda_1 + \lambda_0(1-s)] \tag{15d}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1[B'(1-\alpha-y)+y][\lambda_1 - \lambda_0(1-s) + r\lambda_2] \tag{15e}$$

Consequently, we obtain two relatively simple models of the epoxy–amine reactions based on the amine reactivity scheme given in Fig. 1. The first one obeys the three molecular mechanistic scheme of Horie et al., whereas the second one explores the idea of Flammersheim and Riccardi et al. They are further referred to as ER-model (extended amine reactivity model) and EE-model (extended amine reactivity E· · ·OH equilibrium model), respectively, and will be used to analyze some typical deviations of the experiment from both the overall and reactivity ratio models.

2.5. Multiple equilibrium reactivity ratio models

The assumption that together with the formation of E· · ·OH complexes both A_p and A_s form identical intermediate ones with ether links, respectively $A_p\cdots E_t$ and $A_s\cdots E_t$, leads to the multiple equilibrium scheme (Scheme 6).

The mathematical description of Scheme 6 in a dimension-free form is:

$$K_1^* = \frac{y}{(c_0+\alpha-y)(1-\alpha-y)} \tag{16a}$$

$$K_2^* = \frac{z}{(p-z)(\lambda_1+\lambda_2-z)} = \frac{z'+z''}{(p-z'-z'')(\lambda_1+\lambda_2-z'-z'')} \tag{16b}$$

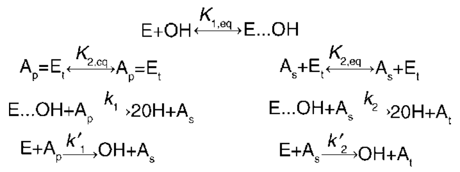
$$-\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = 2K_1[B'(1-\alpha-y)+y](\lambda_1 - z') \tag{16c}$$

$$-\frac{\mathrm{d}\lambda_2}{\mathrm{d}t} = K_1[B'(1-\alpha-y)+y][r(\lambda_2 - z'') - (\lambda_1 - z')] \tag{16d}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1[B'(1-\alpha-y)+y][(\lambda_1 - z') + r(\lambda_2 - z'')] \tag{16e}$$

where z' and z'' are the normalized concentrations of primary and secondary amine hydrogen atoms involved in complexes.

Considering the above equations, we have to note that the averaged equilibrium constant, Eq. (16b), allows determining



Scheme 6.

the variable z being a sum of z' and z'', whereas the numerical solution of the rate equations requires the variables z' and z'' determined separately. In case that K_2^* is an operative equilibrium relation, z' and z'' are easily calculated according to the formulae:

$$z' = \gamma_1 z = \frac{z\lambda_1}{\lambda_1 + \lambda_2} \quad \text{and} \quad z'' = \gamma_2 z = \frac{z\lambda_2}{\lambda_1 + \lambda_2}$$

where $\gamma_1 = \lambda_1/(\lambda_1 + \lambda_2)$ and $\gamma_2 = \lambda_2/(\lambda_1 + \lambda_2)$ are dynamic weighing coefficients.

Consequently, Eq. (16) describe the simultaneous formation of $E\cdots OH$, $A_1\cdots E_t$ and $A_2\cdots E_t$ equilibrium complexes in an exact explicit form, i.e. there is no approximate solution of the variables after each integration step.

For example, at $t = 0$, we have $\alpha = 0$, $\lambda_1 = 1$, $\lambda_2 = 0$, $y = y_0$ and $z = z' = z_0$. When we start to integrate up to $t = t_1$, then: (i) we obtain α, λ_1 and λ_2; (ii) we calculate $\gamma_1 = \lambda_1/(\lambda_1 + \lambda_2)$ and $\gamma_2 = \lambda_2/(\lambda_1 + \lambda_2)$; (iii) we calculate y (from the parabolic equation of K_1^*) and z (from the parabolic equation of K_2^*); (iv) we calculate $z' = \gamma_1 z$ and $z'' = \gamma_2 z$; (v) we are ready to integrate within the next time step according to Eq. (16c) through Eq. (16e) since we have determined all the variables, i.e. there is no iterate approximation.

If primary and secondary amine hydrogen atoms form different strength equilibrium covalent bond complexes, then there must be defined two separate equilibrium constants, viz.

$$K_p^* = \frac{z'}{(p - z' - z'')(\lambda_1 - z')} \quad \text{and}$$

$$K_s^* = \frac{z''}{(p - z' - z'')(\lambda_2 - z'')}$$

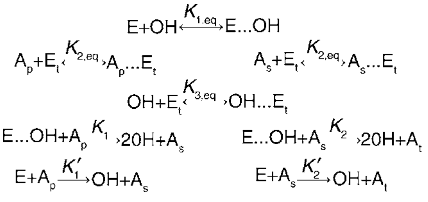
As one can see, the variables z' and z'' are cross-correlated. A simple approximate solution of these variables can be drown within Eq. (16b), viz.

$$z' = \gamma_1 z = \frac{zf\lambda_1}{f\lambda_1 + \lambda_2} \quad \text{and} \quad z'' = \gamma_2 z = \frac{z\lambda_2}{f\lambda_1 + \lambda_2}$$

where the ratio f must be set inversely proportional to r, but both f and r should be supposed to be far from zero and infinity.

The formation of $A_1\cdots E_t$, $A_2\cdots E_t$, $OH\cdots E_t$ and $E\cdots OH$ intermediate equilibrium complexes can be depicted in another multiple equilibrium scheme (Scheme 7).

The mathematical description of Scheme 7 has to account an additional equilibrium between OH and E_t groups, but its final form is similar to that derived following Eq. (16), viz.



Scheme 7.

$$K_1^* = \frac{y}{(c_0 + \alpha - y - v)(1 - \alpha - y)} \tag{17a}$$

$$K_2^* = \frac{z}{(p - z - v)(\lambda_1 + \lambda_2 - z)} \tag{17b}$$

$$K_3^* = \frac{v}{(p - z - v)(c_0 + \alpha - y - v)} \tag{17c}$$

$$-\frac{d\lambda_1}{dt} = 2K_1[B'(1 - \alpha - y) + y](\lambda_1 - z') \tag{17d}$$

$$-\frac{d\lambda_2}{dt} = K_1[B'(1 - \alpha - y) + y][r(\lambda_2 - z'') - (\lambda_1 - z')] \tag{17e}$$

$$\frac{d\alpha}{dt} = K_1[B'(1 - \alpha - y) + y][(\lambda_1 - z') + r(\lambda_2 - z'')] \tag{17f}$$

where v is the normalized concentration of hydroxyl groups involved in $OH\cdots E_t$ complexes.

To solve Eq. (17) one must pay attention on the fact that y and v (or z and v) are correlated variables within the equilibrium relations, respectively K_1^* and K_3^* (or K_2^* and K_3^*), as well as to have in mind that z is a composed variable.

The multiple equilibrium reactivity ratio models, which will be further referred to as ME-models express more complicated but possible mechanistic schemes. In spite of the different physical–chemical nature, the so-called EE-model and ME-models appear quite similar from a purely mathematical point of view.

The above analysis illustrates the main problems of the multiple equilibrium schemes, namely: (i) each equilibrium relation introduces an additional variable; if one considers different covalent bond complexes of A_p and A_s with some other reactive or non-reactive groups then the variable number is doubled and (ii) some equilibrium constants cause correlation between the variables which has to be taken into account if complicated multiple equilibrium schemes of the epoxy–amine reaction will have been tested [50,57].

In our opinion, some equilibrium constants can be ignored on a theoretical basis. For example, the multiple equilibrium scheme of Swier and Van Mele [57] describing simultaneous formation of $E\cdots OH$ and $E\cdots A$ complexes will be valid only within their assumption that the initiation is a catalytic reaction. According to the activated complex theory, the $E\cdots A$ complexes will attempt to overcome the barrier or they will rapidly decompose to reactants, i.e. the lifetime of $E\cdots A$ complexes will be effectively zero if the initiation is a first-order decomposition or a second order reaction. This statement seems to follow from the rate-constant definition according to the theory. Hence, the $E\cdots A_p$ and $E\cdots A_s$ complexes have to be eliminated by accepting a non-catalytic initiation. As pointed out by Xu et al. [17], the $A_1\cdots OH$ and $A_2\cdots OH$ complexes can be supposed to be unimportant.

3. Discussion

We have recently studied the kinetics of the reaction of diglycidyl ether of bisphenol A (DGEBA) with *m*-phenylene diamine (mPDA) [21,52,53]. The experimental DSC kinetics of stoichiometric DGEBA–mPDA formulations has been performed in isothermal and programmed temperature modes following the overall autocatalytic model of the form:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (K_1' + K_1\alpha)(1-\alpha)^n = K_1(B+\alpha)(1-\alpha)^n \qquad (18)$$

It has been observed that this formal velocity equation described fairly well the reaction, i.e. there was no need to use the mostly debatable four parameter model, see Eq. (5). The same finding has been established considering the reaction of DGEBA with diamino diphenyl methane (DDM) as well as that of DGEBA with the mixture of mPDA and DDM [71].

Applying a four-step kinetic approach in programmed temperature mode, we showed that experiments obeyed the three molecular overall model of Horie et al. or $n = 2$. The velocity equation of the DGEBA–mPDA reaction in stoichiometric proportions of the components has been thus evaluated [52], viz.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 3.13 \times 10^6 \exp\left(\frac{50.5\,\mathrm{kJ\,mol^{-1}}}{RT}\right) \times (0.025+\alpha)(1-\alpha)^2\,\mathrm{s}^{-1} \qquad (19)$$

Accepting an identical approach in isothermal mode, we have evaluated a lower than three model of the same reaction, i.e. $n = 1.5$–1.6 [53]. At the same time, both the apparent activation energy determined using iso-conversional methods, E_{ap}, and activation energy extracted from the autocatalytic rate constant according to the model, $E_{\mathrm{a(auto)}}$, were found nearly equal in two DSC modes: $E_{\mathrm{ap}} = 52$–$54\,\mathrm{kJ\,mol^{-1}}$ and $E_{\mathrm{a(auto)}} = 50$–$51\,\mathrm{kJ\,mol^{-1}}$. The small difference between them yielded a slightly higher E_{a} value of the initiation reaction, i.e. $E_{\mathrm{a(non)}} = 58$–$59\,\mathrm{kJ\,mol^{-1}}$.

Considering the equality of E_{ap} and $E_{\mathrm{a(auto)}}$ similar results have been obtained for the kinetics of DGEBA–DDM reaction although some differences from that of DGEBA with mPDA have been established. The non-isothermal kinetics of both reactions has been characterized in comparison using the values of α_{p} (degree of conversion at the maximal reaction rate) and n (power exponent in Eq. (18)). It has been obtained [52,53,71]:

- $\alpha_{\mathrm{p}} = 0.475$–$0.485$ and $n \approx 1.8$ (for the reaction of DGEBA with DDM);
- $\alpha_{\mathrm{p}} = 0.450$–$0.455$ and $n \approx 2.0$ (for the reaction of DGEBA with mPDA).

The isothermal kinetics has yielded more significant differences, viz.

- $\alpha_{\mathrm{p}} = 0.42$–$0.43$ and $n \approx 1.1$ (for the reaction of DGEBA with DDM);
- $\alpha_{\mathrm{p}} = 0.350$–$0.355$ and $n \approx 1.6$ (for the reaction of DGEBA with mPDA).

To explain the above discrepancy, which appears to be typical in the epoxy–amine kinetics, we have tried to describe the isothermal advance of DGEBA–mPDA reaction using the ER-model. It has been rearranged for stoichiometric system into the following set of velocity ODE [21]:

$$-\frac{\mathrm{d}\lambda_0}{\mathrm{d}t} = 4K_1 s(B+\alpha)(1-\alpha)\lambda_0 \qquad (20\mathrm{a})$$

$$-\frac{\mathrm{d}\lambda_1}{\mathrm{d}t} = 2K_1(B+\alpha)(1-\alpha)[\lambda_1 - \lambda_0(1-s)] \qquad (20\mathrm{b})$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1(B+\alpha)(1-\alpha)\,[\lambda_1(1-r) + r(1-\alpha) - \lambda_0(1-s)] \qquad (20\mathrm{c})$$

Since λ_2 can be obtained from the mass balance equations, viz., $\lambda_2 = 1 - \alpha - \lambda_1$, the secondary amine rate expression has been eliminated.

The data have been fitted according to the boundary models at $r = 1$ or, alternatively, at $s = 1$. Note that if $r = 1$ and $s = 1$, then Eq. (20) are reduced to the overall model of Horie et al. an evaluated form of which is Eq. (19). The results showed sufficiently good description when $s = 0.67$ (if $r = 1$) or $r = 2.0$ (if $s = 1$). It has been concluded that infinite couple of values of the two parameters would also describe the isothermal DSC experiments.

As we discuss below, combining the isothermal and non-isothermal DSC techniques might be turn out important in the study of the mechanistic kinetics of epoxy–amine reactions.

A test of the boundary models in programmed temperature mode is shown in Figs. 2 and 3. The simulated curves according to the overall model, Eq. (19), are presented in comparison. The boundary model predictions in Fig. 2a and b depict the degree of epoxy conversion curves whereas those in Fig. 3a and b illustrate the secondary amine consumption curves.

The simulations in all figures have been performed using the parameters of Eq. (19), as extracted in non-isothermal mode [52] and the best fit values of r and s determined by isothermal experiments [53], i.e. in this study, we exhibit the effect of parameters on the reaction behaviour instead of the best fit figures; the lasts will be discussed later in this series.

The data in Fig. 2a and b show that the two boundary models describe in different manner the reaction in time and temperature scales. An increase of r moves the non-isothermal DSC curve left, or the reaction appears accelerated in the temperature scale compared to that predicted by the evaluated overall model; a decrease of s transposes the DSC peak at higher temperatures or the reaction appears retarded. The deviation between the curves simulated according to the

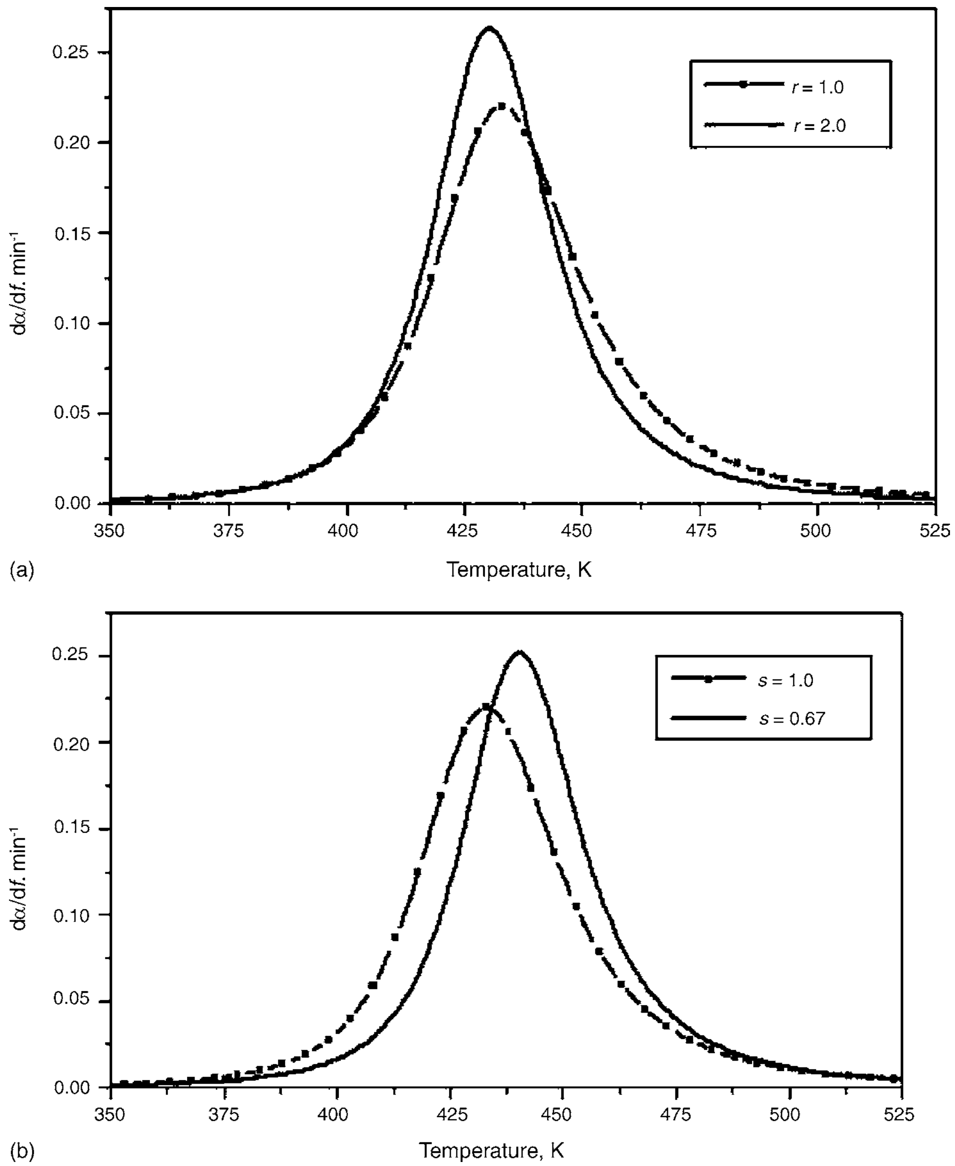


Fig. 2. (a) Non-isothermal DSC curves simulated according to the boundary *r*-model, Eq. (20), at $s = 1$ and the evaluated overall model of Horie et al., Eq. (19); $dT/dt = 10\,K\,min^{-1}$. (b) Non-isothermal DSC curves simulated according to the boundary *s*-model, Eq. (20), at $r = 1$ and the evaluated overall model of Horie et al., Eq. (19); $dT/dt = 10\,K\,min^{-1}$.

boundary models decreases with heating rate. At a constant temperature they almost coincide.

The above analysis points out that there must be a single couple of r and s values which can predict the reaction progress both in isothermal and programmed temperature modes. A fairly good description of the experiment has been obtained at $r \approx 1.4$ and $s \approx 0.8$. In spite of the good description, this value of r implies a positive KSE for the reaction of DGEBA with mPDA that seems to be under consideration. The results in literature indicate equal reactivity of the primary and secondary amines [29] or a slightly negative KSE [23].

Fig. 3a and b shows the λ_2 curves simulated in programmed temperature regime. As one can see, the maximum of these curves (at $\alpha \approx 0.5$) is sensitive concerning the parameter values, i.e. having this data one can confirm or reject the ER-model. The same finding has been established by Paz-Abuin et al. who studied the epoxy–amine kinetics using near-FTIR [34].

Our analysis of the reaction kinetics of DGEBA with mPDA and DDM as well as with their mixture performed using the ER-model points out that a more sophisticated model is probably required to describe it correctly. In our opinion, it has to be based on the original approach of Flammersheim–Riccardi due to the following reasons:

- The E. . .OH equilibrium effectively decreases the reaction order, i.e. the predicting capabilities of EE-model and ME-models (considering experiments that exhibit higher values of α_p) are higher than the classical model predictions.

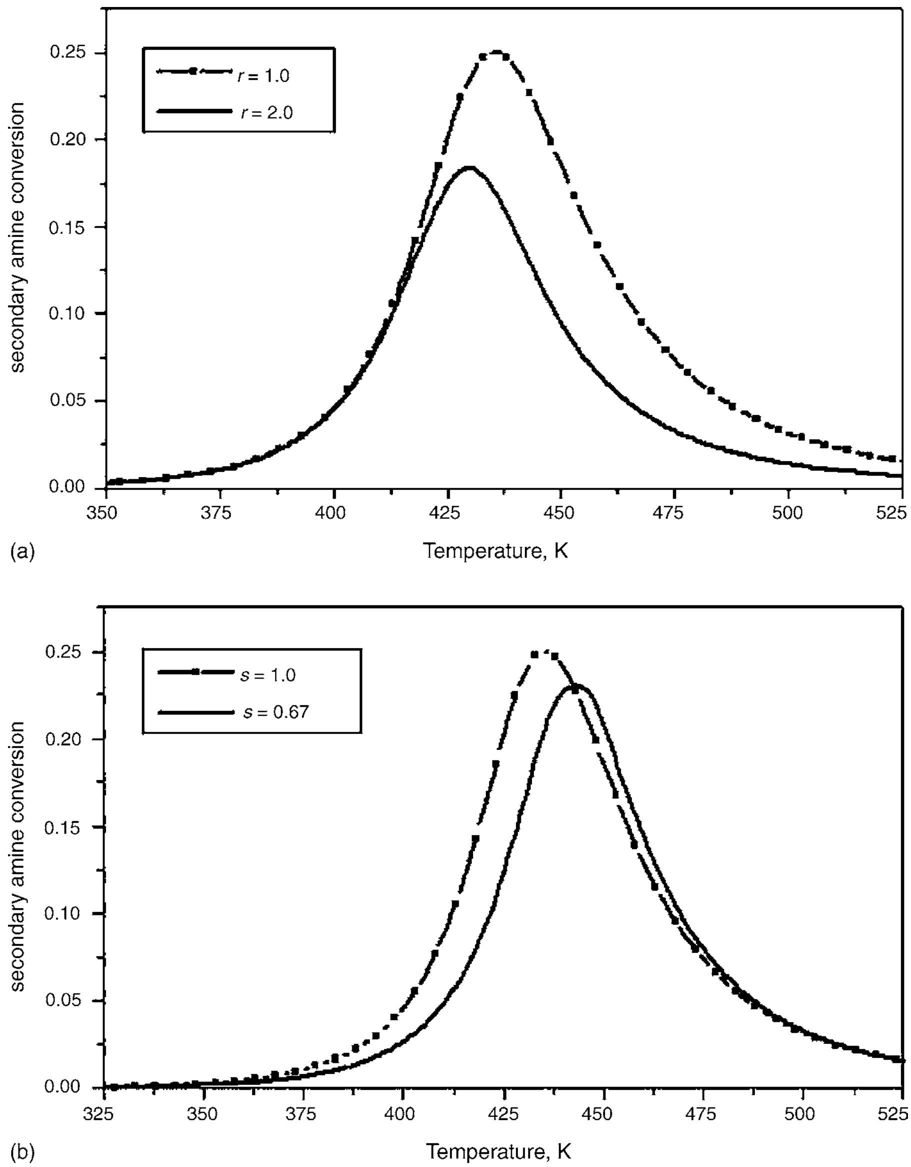


Fig. 3. (a) Non-isothermal λ_2 curves simulated according to the boundary *r*-model, Eq. (20), at $s = 1$ and the evaluated overall model of Horie et al., Eq. (19); $dT/dt = 10\,K\,min^{-1}$. (b) Non-isothermal λ_2 curves simulated according to: the boundary *s*-model, Eq. (20), at $r = 1$ and the evaluated overall model of Horie et al., Eq. (19); $dT/dt = 10\,K\,min^{-1}$.

- In contrast to E...OH equilibrium causing accelerated rates, the non-reactive equilibrium complexes (or an appropriate couple of *r* and *s* values) can well describe the reaction delay, especially in the temperature scale, as the modelling example indicate.

In this study, we have attempted to extract two alternative mathematical descriptions of the epoxy–amine addition applying the fundamental idea of these authors who postulated that the rate-determining step of the reaction overcomes the formation of an intermediate equilibrium E...OH complex. To do this, the below presented approximations have been accepted:

- The rate constants $K_i (i = 1, 2)$ and equilibrium relations K_j^* ($j = 1$–3) express the velocity equations in terms of reacting groups; they are associated with corresponding kinetic parameters.
- The parameters *r* and *B* are simple rate-constant ratios, i.e. $r = K_2/K_1 = K_2'/K_1'$ and $B = K_1'/K_1 = K_2'/K_2$.
- The KSE is not temperature influenced, i.e. *r* is a temperature-independent parameter during the reaction advance—in line with the existing experimental findings [6,12,16,20,34–36].

In stoichiometric proportions of the reaction components, the secondary amine rate expression can be again omitted. Thus, the EE-model is rearranged to:

$$K^* = \frac{y}{(1 - \alpha - y)(c_0 + \alpha - y)} \tag{21a}$$

$$-\frac{d\lambda_0}{dt} = 4K_1 s[B'(1-\alpha-y)+y]\lambda_0 \quad (21b)$$

$$-\frac{d\lambda_1}{dt} = 2K_1[B'(1-\alpha-y)+y][\lambda_1-\lambda_0(1-s)] \quad (21c)$$

$$\frac{d\alpha}{dt} = K_1[B'(1-\alpha-y)+y] \times [(1-r)\lambda_1 + r(1-\alpha) - \lambda_0(1-s)] \quad (21d)$$

Based on the above assumptions, the EE-model expresses a more simplified scheme, which has been obtained by implementing the extended amine reactivity scheme (a four-rate-constant model is also available [63]) into the original model of Flammersheim and Riccardi et al. It has been additionally accounted that the amine monomer, the remaining primary amine hydrogen atoms, and the secondary amine hydrogen atoms do not alter the E$\cdots$OH equilibrium, although they might exhibit different reactivity. In terms of the below discussed multiple equilibrium schemes, it can be suggested that some equilibrium constants are either vanishing or linearly contributing to other effects (e.g. steric hindrances) thus describing different strength transition state complexes in regard to the corresponding amine functionalities. In our opinion, some arbitrariness of the rate-constant ratio definitions is compensated by the analytical dependences originating from the EE-model, as is commented below.

Deriving the extended reactivity ratio model, Eq. (20), we have shown that the variables α and λ_1 are explicit functions of λ_0 [21]. The same dependences can be obtained from Eq. (21), viz.

$$\lambda_1 = (1-p')\lambda_0 + p'\lambda_0^{1/2s} \quad (22)$$

$$\alpha = 1 - \left\{(1-p'')(1-p')\lambda_0 + \frac{p'(1-r)}{2-r}\lambda_0^{1/2s} + \left[p''(1-p') + \frac{p'}{2-r}\right]\lambda_0^{r/4s}\right\} \quad (23)$$

where $p' = 1/2(1–1/2s)$ and $p'' = 1/2(1–r/4s)$.

It is easily established that if $s=1$, then $p'=1$, and λ_1 becomes simple square root function of λ_0. At the same time, Eq. (23) is reduced to:

$$\alpha = \frac{1-[\lambda_0^{1/2}(1-r)+\lambda_0^{r/4}]}{(2-r)} \quad (24)$$

Having in mind that $\lambda_1 = (\lambda_0)^{1/2}$, then Eqs. (24) and (13) exactly coincide.

The above-presented dependences might be successfully applied in the study of the epoxy–amine reactions. For example, using the near-FTIR technique Paz-Abuin et al. have determined the reactivity ratio at the maximum of λ_2 curves, where $d\lambda_2/dt = 0$ and $r = \lambda_1/\lambda_2$ [34]. Following Eq. (13) one can test the dependence of α versus λ_1 and to derive the plot of r versus α in the whole conversion range. If one will observe significant deviation from linearity according to Eq. (13), especially, within the range $\alpha = 0-0.3$, then the experimental data are preferable to be fitted iteratively using Eq. (23).

On the other hand, these integral time-independent functions allow performing comparative kinetics studies of epoxy–amine reactions considering the reactivity ratio and applying different measuring techniques, for instance–HPLC and near-FTIR. As it is known, the definition of λ_1 according to the former is $\lambda_1 = (\lambda_0)^{1/2}$, whereas λ_1 is a direct measure by near-FTIR method. If one will have significant discrepancy concerning the r values determined by both methods, then it can be assigned to the variable definition. Hence, the use of Eqs. (22) and (23) seems to be reasonable.

Based on the listed assumptions the multiple equilibrium scheme described with the aid of Eq. (17) can be simplified in stoichiometric proportions of the reaction components into a set of the following velocity ODE:

$$K_1^* = \frac{y}{(c_0+\alpha-y-v)(1-\alpha-y)} \quad (25a)$$

$$K_2^* = \frac{z}{(p-z-v)(\lambda_1+\lambda_2-z)} \quad (25b)$$

$$K_3^* = \frac{v}{(p-z-v)(c_0+\alpha-y-v)} \quad (25c)$$

$$-\frac{d\lambda_1}{dt} = 2K_1[B'(1-\alpha-y)+y](\lambda_1-z') \quad (25d)$$

$$\frac{d\alpha}{dt} = K_1[B'(1-\alpha-y)+y][(1-r)(\lambda_1-z') + r(1-\alpha-z)] \quad (25e)$$

If $K_3^* = 0$ and $v = 0$, then Eq. (25) become a simplified form of Eq. (16), i.e. the $E_t\cdots$OH complexes in this case are supposed to be unimportant.

The multiple equilibrium schemes, which have been basically suggested by Swier and Van Mele [57] can be discussed in terms of the theory of solutions [72]. According to this theory all above-presented interactions are possible to exist in each ideally miscible binary mixture. They facilitate the solubility, accounted by the well-known parameter of Flory–Huggins and the strength of these covalent bonds is of the order of one to several tenth kJ mol^{-1} [4]. Having this in mind, we suppose that some equilibrium constants in the presence of a chemical reaction should be less than those in a non-reactive mixture. In our opinion, it is scarcely to imagine that E$\cdots$OH complexes attempting to form E$\cdots$OH$\cdots$A transition state complexes (and leading to formation of chemical bonds with strength exceeding a hundred kJ mol^{-1}) will not break up some A$\cdots E_t$ covalent bonds (the strength of which is two orders less).

Considering the commented differences in the formal DSC kinetics of DGEBA with mPDA and DGEBA with DDM, we will show in the next studies that the mechanistic kinetics of these similar reactions according to EE-model and ME-models is also different, especially in regard to the equilibrium constant K_1^*. Although both models will be applied to study the more complicated kinetics of the epoxy–amine addition the use of EE-model is preferable, at least as a first step. In our opinion, this is due to the following reasons.

The first one is obvious from the analytical form of Eq. (21) involving a minimal amount of adjustable parameters in comparison to the experimentally measured variables. The second one consists in the fact that the diffusion-controlled kinetics is easily accounted from mathematical point of view. The diffusion-controlled term introduced in the rate constant K_1 explicitly modifies all other ones through the ratios B', r and s. The analytical dependences originating from the EE-model indicate its third important advantage.

4. Conclusions

The mechanistic models of the epoxy–amine addition based on the assumption that the rate-controlling step of the reaction overcomes the formation of an intermediate epoxy–hydroxyl bimolecular complex have been classified in comparison with the models described within the scheme of Horie et al.

Two alternative mechanistic derivations optimized against the parameter and variable number have been proposed. The first one has been obtained by combining an extended amine reactivity and epoxy–hydroxyl equilibrium schemes. The second description has been derived with the aid of a multiple equilibrium scheme differing from those known in literature.

The models are presented in a convenient dimension-free form suitable for a direct use of the routine ODE solver programs–for example, see Ref. [73].

A modelling example in programmed temperature mode performed using a model within the classical scheme has been discussed. In spite of the ability of the last to describe the reaction kinetics of DGEBA with mPDA almost perfectly, the reactivity ratio value appeared unreliable.

It has been suggested that more reliable explanations of the deviations from the overall model might be achieved by using the intermediate equilibrium models due to mainly the decrease of the reaction order. They will be further tested but, prior to this, a theoretical analysis concerning the effect of parameters on the model performance will be also carried out.

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