A New Approach to Modeling the Cure Kinetics of Epoxy Amine Thermosetting Resins. 1. Mathematical Development

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Received July 31, 1990; Revised Manuscript Received November 9, 1990

ABSTRACT: The Horie model for describing the cure kinetics of epoxy amine systems is extended to explicitly include the etherification reaction, which becomes significant when there is an excess of epoxy with respect to amine and when the cure is performed at higher temperatures. A solution to the kinetic equations is derived that makes it possible to determine the relationship between the degree of conversion α and the rate of conversion $d\alpha/dt$. Different possible mechanisms for the etherification reaction are considered. The model can be used to calculate the amounts of different groups formed in the reaction and hence provide information concerning the network structure.

Introduction

The widespread use of epoxy-based composites in the aerospace industry, coupled with the growth of computer-aided design and manufacturing, has resulted in increased interest in modeling the processing of these materials.[1] The object is to optimize the processing parameters in order to consistently obtain high-quality parts and to minimize the experimental work required to design a cure cycle for any new parts that may be introduced. With a good model, it is possible to predict how the system will behave during cure and what its final condition will be. One of the most important components of such a model is an accurate description of the cure kinetics. However, the chemistry involved in the epoxy curing process is rather complex, and in spite of the extensive research that has been done over the years it is still not completely understood. As a result, it is virtually impossible to describe it rigorously, and existing models always involve certain assumptions and approximations.

Many commercial composite systems consist of amine-cured epoxy resins. The epoxy amine reaction produces hydroxyl groups, which have two effects: (1) they catalyze the reaction that produces them and (2) they themselves can react with epoxy rings to form ether linkages. The progress of the curing reaction is described quantitatively in terms of the fractional degree of conversion of epoxide groups, usually designated α. To model the kinetics it is necessary to derive an equation expressing $d\alpha/dt$, the rate of change of α with time, as a function of α and the temperature T. In 1970, Horie et al.,[2] making use of mechanisms proposed by earlier workers, developed an equation to describe the kinetics of the reaction between epoxy and primary amine. If it is assumed that the secondary amine groups formed in the reaction show the same degree of reactivity toward epoxy groups as the primary amine groups initially present, their equation simplifies to

$$d\alpha/dt = (K_1 + K_2\alpha)(1 - \alpha)(B - \alpha) \qquad (1)$$

where K_1 is a rate constant for the reaction catalyzed by groups initially present in the resin, K_2 is a rate constant for the reaction catalyzed by newly formed hydroxyl groups, and B is the initial ratio of amine N–H bonds to epoxide rings. Thus this equation takes into account the autocatalytic nature of the epoxy amine reaction, but it does not allow for the possibility of other reactions that produce ether groups ("etherification"). It was found to fit experimental data well at low levels of conversion, up to $\alpha = 0.5$ or so.[2,3] The deviations observed beyond this point were attributed to the onset of diffusion control as a result of gelation of the system.

Many aerospace materials contain aromatic amines, which require higher curing temperatures than aliphatic ones. Furthermore, there is often a significant excess of epoxy with respect to amine. Under these circumstances, the etherification reaction becomes more important and the Horie approach is less valid. Attempts to include the etherification reaction complicate the mathematics considerably, so an exact solution of the kinetic equations has not been obtained. In order to model cases where the Horie equation is inadequate, Kamal and co-workers developed the following semiempirical modification:[4]

$$d\alpha/dt = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (2)$$

The introduction of the variable exponents m and n usually makes it possible to obtain a good fit to experimental data, and this equation has found wide successful application for both epoxy and polyester systems. However, it does not explicitly take into account the etherification reaction, so it does not provide a clear description of the curing process and its chemistry, which is important for understanding the network formation process. The exponents m and n are often found to be temperature-dependent, so the dependency must be determined over the whole range of temperatures of interest.

Recently there have been a few attempts to include the etherification reaction in the analysis.[5-10] While these have not made the assumption that the primary and secondary amine groups show the same reactivity, they have made certain other assumptions and approximations in order to perform the analysis. For instance, Zukas et al.[5] assumed that, like the epoxide–amine reaction, the epoxide–hydroxyl reaction involves two rate constants (corresponding to "uncatalyzed" and hydroxy-catalyzed reactions) and that their ratio is the same as for the epoxide–amine reaction. In order to obtain an acceptable fit to their data, they had to introduce semiempirical modifications such as letting some of the apparent reaction orders deviate from 1 or even vary with the degree of cure α. Riccardi and Williams[7,8] used a similar mechanism but a different mathematical treatment to study a different system. They obtained a good fit to their data but some of the rate constants, including those for etherification, were difficult to determine with good accuracy because the data were not sufficiently sensitive to them. Other workers have assumed a simple epoxide–hydroxyl reaction as the etherification mechanism.[9,10] Chern and Poehlein, in their

0024-9297/91/2224-3093$02.50/0 Published 1991 by the American Chemical Society

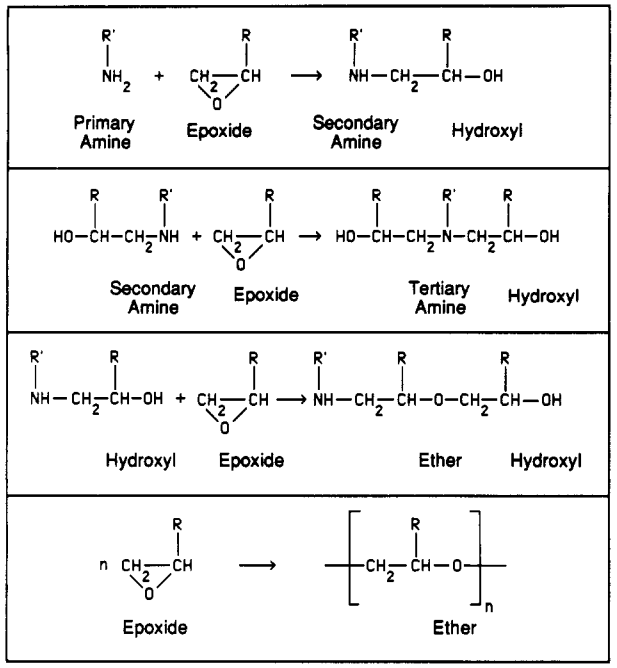

Figure 1. Main reactions involved in the cure of epoxy resins with primary amine curing agents.

analysis,[9] determined only the rate constant for the reaction between epoxide and primary amine; all others were expressed as a fixed multiple of this one based on data taken from the literature for similar systems. Chiao[10] also used data from other systems in order to fix the ratio of certain pairs of rate constants. Although a good fit and reasonable results were obtained, the transfer of such data from one system to another is subject to question, given that some of the rate constants are dependent on the amount of catalytic impurities in the particular system.

In this paper, an alternative approach to solving the kinetic equations is developed, in which the Horie treatment is extended to include the etherification reaction. Although a simple equation relating $d\alpha/dt$ to α cannot be obtained, it will be shown that it is possible to indirectly determine the exact relationship between the two. Different possible mechanisms for the etherification reaction are considered, either involving or not involving hydroxyl and tertiary amine groups.

Model Development

Epoxy Reactions. The cure of epoxy amine systems has been reviewed by Barton[11] and Rozenberg.[12] For a primary amine curing agent, the main reactions that occur are illustrated in Figure 1. Their relative importance has been the subject of much research, but the situation is far from clearly understood. The first reaction, which occurs quite readily, is between an epoxide ring (E) and a primary amine group (PA) to produce a link containing a secondary amine group (SA) and a hydroxyl group (OH). The secondary amine group formed in this reaction can react further to give a tertiary amine group (TA) and a new hydroxyl group. As mentioned above, both of these reactions have been shown to be catalyzed by hydroxyl groups. Another reaction that can occur is that between an epoxide ring and a hydroxyl group to form an ether link and a new hydroxyl group, which is then available for further reaction. The epoxide–hydroxyl reaction is generally slower than the epoxide–amine reaction and becomes important only when the cure is performed at high temperatures or when there is an excess of epoxy with respect to amine.[11] The situation regarding the reaction between

Table I
Symbols Used in the Kinetic Analysis

group	representation	concn at time t	concn at $t = 0$
epoxide	E	E	E_0
hydroxyl	H	H	H_0
primary amine	A_1	A_1	A_{10}
secondary amine	A_2	A_2	0
tertiary amine	A_3	A_3	A_{30}
ether	ether	[ether]	0
"impurity" catalyst	X	X	X

epoxide and secondary amine is less clear. There is evidence that the secondary amine groups react at the same rate as the primary ones, but there is also evidence that they react significantly more slowly.[12,13]

Even if no reactive amine is present, epoxy resins will polymerize on their own if heated to a sufficiently high temperature. This is attributed to a "homopolymerization" reaction, which may be initiated by impurity groups present in the resin or by (nonreactive) tertiary amine groups. It is generally considered to be difficult to achieve unless specific catalysts such as boron trifluoride complexes are present.

Kinetic Equations. The resin system may be considered as a collection of epoxide groups, amine groups, hydroxyl groups, ether groups, and catalysts. The various species and their concentrations may be represented by the symbols shown in Table I. We assume that the unreacted resin contains only epoxide, primary and tertiary amine, hydroxyl, and catalyst (other than hydroxyl) groups. The primary amine groups come from the curing agent. Tertiary amine groups may be present as part of the epoxy molecule, so an initial concentration term A_{30} is included to allow for their presence; such is the case, for example, in the well-known commercial product TGDDM (bis[4-(diglycidylamino)phenyl]methane). The "unknown" catalyst X represents impurities that may be present in the resin; the concentration is taken to be constant. The proposed reaction scheme is as follows:

$$\mathrm{E} + \mathrm{A}_1\,(+\,\mathrm{H}) \xrightarrow{k_1} \mathrm{A}_2 + \mathrm{H}\,(+\,\mathrm{H})$$

$$\mathrm{E} + \mathrm{A}_1\,(+\,\mathrm{X}) \xrightarrow{k'_1} \mathrm{A}_2 + \mathrm{H}\,(+\,\mathrm{X})$$

$$\mathrm{E} + \mathrm{A}_2\,(+\,\mathrm{H}) \xrightarrow{k_2} \mathrm{A}_3 + \mathrm{H}\,(+\,\mathrm{H})$$

$$\mathrm{E} + \mathrm{A}_2\,(+\,\mathrm{X}) \xrightarrow{k'_2} \mathrm{A}_3 + \mathrm{H}\,(+\,\mathrm{X})$$

$$\mathrm{E} + m\mathrm{H} + n\mathrm{A}_3 \xrightarrow{k_3} \text{ether} + m\mathrm{H} + n\mathrm{A}_3$$

The first equation describes the reaction between an epoxide group and a primary amine group to form a secondary amine group and a new hydroxyl group. It is catalyzed by hydroxyl groups, H. These participate in the reaction but remain unchanged, so they are shown in parentheses. The second equation describes the same reaction but catalyzed by groups X initially present in the system. The third and fourth equations are similar, except that they refer to the reactions between epoxide and secondary amine groups to form tertiary amine and hydroxyl groups. The first four equations are equivalent to those used by Horie.[2] The fifth is new and represents the etherification reaction. In the following treatment, we use the term etherification to refer to both the epoxide–hydroxyl reaction and the homopolymerization reaction. In both cases, the net result is the same: an epoxide ring is transformed into an ether linkage and there is no change

Table II
Coefficients in Equation 30 Corresponding to Different Possible Mechanisms for the Etherification Reaction (Equation 8)

term	m	n	C_1	C_2	C_3	C_4
E	0	0	0	0	1	-1
EH	1	0	0	0	$Y-R$	$-(Y+1)$
EH^2	2	0	$-(R+1)$	0	$(Y-R)^2$	$-(Y+1)^2$
EA_3	0	1	$-(R+1)$	0	$Z+R^2$	$-(Z+1)$
EHA_3	1	1	$(R+1)(R-Y-1)$	$-1/2(R+1)$	$(Z+R^2)(Y-R)$	$-(Z+1)(Y+1)$

in the number of hydroxyl groups. However, in the first case one hydroxyl group is destroyed and another is formed. In the second case, hydroxyl groups do not participate. To cover the different possibilities, the equation is written in a general form with coefficient "m" representing the number of hydroxyl groups involved (as either reactant or catalyst) and "n" the number of tertiary amine groups (as catalyst). Both m and n could be zero. (These exponents m and n should not be confused with those used in eq 2.) The kinetic equations for the above reaction scheme are as follows:

$$dE/dt = -k_1HEA_1 - k'_1XEA_1 - k_2HEA_2 - k'_2XEA_2 - k_3EH^mA_3^n \quad (3)$$

$$dA_1/dt = -k_1HEA_1 - k'_1XEA_1 \quad (4)$$

$$dA_2/dt = +k_1HEA_1 + k'_1XEA_1 - k_2HEA_2 - k'_2XEA_2 \quad (5)$$

$$dA_3/dt = +k_2HEA_2 + k'_2XEA_2 \quad (6)$$

$$dH/dt = +k_1HEA_1 + k'_1XEA_1 + k_2HEA_2 + k'_2XEA_2 \quad (7)$$

$$d[\text{ether}]/dt = +k_3EH^mA_3^n \quad (8)$$

The k_3 term in eqs 3 and 8 arises from the etherification reaction. It is assumed to be first order with respect to epoxide concentration, but the exponents m and n may be 0, 1, or 2, depending on the other species participating in the reaction. By manipulation of eqs 3–8, it should be possible to solve for the concentration of all six components as a function of time. The concentration of catalytic impurities, X, is unknown but is assumed to remain constant throughout the cure. Thus the quantities k'_1X and k'_2X could be replaced by constants k''_1 and k''_2, respectively. This is the same formulation that would result if the reaction were assumed to be uncatalyzed, so as far as the mathematical development is concerned, it does not matter whether the reaction is considered to be uncatalyzed, X-catalyzed, or both.

Solution of the Equations. There are three material balance constraints inherent in these equations. First, the loss of one N–H bond always results in the formation of one O–H bond, so the total number of N–H bonds plus O–H bonds is constant. Thus

$$2A_1 + A_2 + H = \text{constant} = 2A_{10} + H_0$$

so that

$$A_2 = 2A_{10} + H_0 - 2A_1 - H \quad (9)$$

Second, the total number of nitrogen atoms is constant, so that

$$A_1 + A_2 + A_3 = \text{constant} = A_{10} + A_{30}$$

and

$$A_3 = A_{30} + A_{10} - A_1 - A_2$$

Substituting for A_2 from eq 9 gives

$$A_3 = A_{30} + A_1 - A_{10} + H - H_0 \quad (10)$$

Third, the total number of oxygen atoms is constant, so

$$E + H + [\text{ether}] = \text{constant} = E_0 + H_0$$

and

$$[\text{ether}] = E_0 + H_0 - E - H \quad (11)$$

On substituting eqs 9 and 10 into eqs 3, 4, and 7 we are left with the following three equations

$$dE/dt + dH/dt = -k_3EH^m(A_{30} + A_1 + H - A_{10} - H_0)^n \quad (12)$$

$$dA_1/dt + dH/dt = (k'_2X + k_2H)(2A_{10} + H_0 - 2A_1 - H)E \quad (13)$$

$$dA_1/dt = -(k'_1X + k_1H)EA_1 \quad (14)$$

Equations 12–14 involve only three unknowns (E, A_1, and H) and may be solved for these as a function of t. The remaining three unknowns (A_2, A_3, and [ether]) may be obtained from these by means of eqs 9–11. To solve eqs 12–14, it is helpful to make the following transformation to dimensionless variables:

$$\alpha = 1 - \frac{E}{E_0} \quad \text{or} \quad E = E_0(1-\alpha) \quad (15)$$

$$\beta = 1 - \frac{2A_1 + A_2}{2A_{10}} = \frac{H - H_0}{2A_{10}} \quad \text{or} \quad H = H_0 + 2A_{10}\beta \quad (16)$$

$$\gamma = 1 - \frac{A_1}{A_{10}} \quad \text{or} \quad A_1 = A_{10}(1-\gamma) \quad (17)$$

The quantity α is the well-known extent of conversion, as defined in terms of the fraction of epoxide groups reacted. The variable β is the fraction of the N–H bonds that have reacted with epoxide, and since the loss of each N–H bond results in formation of one O–H bond, it is also a measure of the number of hydroxyl groups produced by the reaction. Finally, γ is a measure of the number of primary amine groups reacted. When $t = 0$ (unreacted resin), $\alpha = \beta = \gamma = 0$, and when the reaction is complete $\alpha = \beta = \gamma = 1$. The evolution of these three variables with time completely describes the curing process, since they correspond to the reaction of epoxide with primary amine only (γ), primary plus secondary amine (β), and primary amine plus secondary amine plus hydroxyl (α). We also define the following constants: $B = 2A_{10}/E_0$ = amine-to-epoxide ratio in unreacted resin; $Y = H_0/2A_{10} = H_0/BE_0$ = measure of hydroxyl content in unreacted resin; $Z = A_{30}/A_{10} = 2A_{30}/BE_0$ = measure of tertiary amine content in unreacted resin. On transformation, eqs 12–14 become

$$\frac{d\alpha}{dt} - B\frac{d\beta}{dt} = k_3(BE_0)^{m+n}(Y+\beta)^m((1/2)Z - (1/2)\gamma + \beta)^n(1-\alpha) \quad (18)$$

$$\frac{d\beta}{dt} - \frac{1}{2}\frac{d\gamma}{dt} = \{k'_2 X E_0 + k_2 H_0 E_0 + k_2 E_0^2 B\beta\} \times (\gamma - \beta)(1 - \alpha) \quad (19)$$

$$d\gamma/dt = \{k'_1 X E_0 + k_1 H_0 E_0 + k_1 E_0^2 B\beta\} \times (1 - \gamma)(1 - \alpha) \quad (20)$$

It is impossible to solve these equations without making some simplifications.

Horie et al. made the assumption that the reactivity of the secondary amine groups as compared to that of the primary amine groups is the same for both the X-catalyzed and the hydroxyl-catalyzed reactions. In other words

$$k_2/k_1 = k'_2/k'_1 = r \quad (21)$$

With this assumption, dividing eq 20 into eq 19 leads to

$$\frac{d\beta}{d\gamma} - \frac{1}{2} = r\frac{\gamma - \beta}{1 - \gamma} \quad (22)$$

This may be solved (with the initial condition $\gamma = 0$ when $\beta = 0$) to give

$$\beta = \gamma + \frac{1}{2(1-r)}\{(1-\gamma) - (1-\gamma)^r\} \quad (23)$$

This establishes the relation between β and γ, and makes it possible to eliminate β from eqs 18–20, reducing them to two equations in two unknowns. Unfortunately, an exact solution is still impossible, and to proceed further it is necessary to assume that $r = {}^1/_2$. This implies that the secondary amine N–H bonds react with the epoxide rings as readily as do the primary amine N–H bonds. Since a secondary amine group has only one N–H bond, whereas a primary amine group has two, the probability of reaction is halved. As already mentioned, there is conflicting experimental evidence on this point, with cases where the assumption has been found to be valid and others where it has not.[12,13] When it is valid, eq 23 simplifies to

$$\beta = 1 - (1 - \gamma)^{1/2} \quad \text{or} \quad \gamma = \beta(2 - \beta) \quad (24)$$

On combining eqs 19 and 20 and using this relationship to eliminate γ, we obtain

$$d\beta/dt = (K_1 + BK_2\beta)(1 - \beta)(1 - \alpha) \quad (25)$$

where

$$K_1 = (1/2)E_0(k'_1 X + k_1 H_0) \quad \text{and} \quad K_2 = (1/2)E_0^2 k_1 \quad (26)$$

It should be noted that K_1 combines the effects of catalysis by all groups initially present, both unknown (X) and hydroxyl (H_0). Although not specifically considered here, if any uncatalyzed epoxide–amine reaction were present it would also be included in K_1 and eq 25 would still apply. The second rate constant K_2 corresponds to catalysis by only those hydroxyl groups formed in the reaction.

On eliminating γ from eq 18, we obtain

$$\frac{d\alpha}{dt} - B\frac{d\beta}{dt} = K_3(Y + \beta)^m(Z + \beta^2)^n(1 - \alpha) \quad (27)$$

where

$$K_3 = k_3 2^{-n}(BE_0)^{m+n} \quad (28)$$

We now have a set of two equations (eqs 25 and 27) in two unknowns (α and β). It is still impossible to obtain exact solutions for α and β as a function of t. However, if we divide eq 27 by eq 25, the $(1 - \alpha)$ term cancels out and we obtain

$$\frac{d\alpha}{d\beta} - B = \frac{K_3(Y + \beta)^m(Z + \beta^2)^n}{(K_1 + BK_2\beta)(1 - \beta)} \quad (29)$$

This equation may be solved exactly, using the method of integration by partial fractions, to give α as a function of β. For integral values of m and n with $m + 2n \leq 3$, the term on the right may be expanded in the following form:

$$\left[T_1 + T_2\beta + \frac{T_3}{K_1 + BK_2\beta} + \frac{T_4}{1 - \beta}\right]$$

where the coefficients T_i depend on the particular values of m and n. Such an expression is easily integrated and the solution to eq 29 may be written in the form

$$\alpha = B\beta + \frac{K_3}{K_1 + BK_2}[C_1\beta + C_2\beta^2 + C_3 \ln(1 + R^{-1}\beta) + C_4 \ln(1 - \beta)] \quad (30)$$

where $R = K_1/BK_2$. The initial condition $\alpha = 0$ when $\beta = 0$ has been applied. Expressions for the coefficients C_1, C_2, C_3, and C_4 are given in Table II for five possible combinations of m and n.

Combining eqs 25 and 27 gives

$$d\alpha/dt = [B(K_1 + BK_2\beta)(1 - \beta) + K_3(Y + \beta)^m(Z + \beta^2)^n] \times (1 - \alpha) \quad (31)$$

It is impossible to invert eq 30 to obtain β in terms of α. Consequently, eq 31 cannot be converted into an analytical expression relating $d\alpha/dt$ to α. However, the exact relationship between $d\alpha/dt$ and α can be determined on a point-by-point basis. Thus, for a given set of rate constants (K_1, K_2, K_3) and a given value of β, eq 30 may be used to calculate the corresponding value of α, followed by eq 31 to calculate $d\alpha/dt$. Repeating this procedure for a set of values of β ranging from 0 to 1 gives an exact set of points (α, $d\alpha/dt$), which can be used to plot a curve and compare with experimental data. The rate constants can then be varied until the best match is obtained. Different reaction mechanisms for the etherification reaction can be investigated by using the appropriate values of the exponents m and n, as given in Table II. It should be noted that this procedure allows no control over the particular values of α obtained. If it is desired to calculate the values of $d\alpha/dt$ corresponding to particular values of α, then an alternative procedure can be used in which eq 30 is solved numerically for β and eq 31 is then used to calculate $d\alpha/dt$.

The use of the two variables α and β to model the cure makes it possible to follow quantitatively the two reaction paths, epoxy amine and etherification. The relative importance of these will vary depending on the temperature. Once the three rate constants and their temperature dependence have been determined, the cure can be numerically modeled for any temperature program of interest by using eqs 25 and 31. If the ratio of hardener to epoxy in the resin is changed, in principle this can be taken into account by calculating the changes in B and E_0 and making the appropriate adjustments to K_1, K_2, and K_3 (eqs 26 and 28). It should be noted that eq 30, relating α to β, applies only for the case of isothermal cure, where the rate constants do not change. Its main usefulness lies in analyzing isothermal cure data to determine the rate constants.

The concentrations of the various species involved in the reactions may also be related to α and β, by making use of eqs 9–11, 15–17, and 24. Expressed in terms of the

initial epoxide concentration E_0, these are as follows

Epoxide

$$E/E_0 = 1 - \alpha \tag{32}$$

Hydroxyl

$$H/E_0 = B(Y + \beta) \tag{33}$$

Primary amine

$$A_1/E_0 = (1/2)B(1 - \beta)^2 \tag{34}$$

Secondary amine

$$A_2/E_0 = B\beta(1 - \beta) \tag{35}$$

Tertiary amine (formed in reaction)

$$A_3/E_0 = (1/2)B\beta^2 \tag{36}$$

Ether

$$[\text{ether}]/E_0 = \alpha - B\beta \tag{37}$$

Equations 25 and 30–37 thus allow a complete description of the curing process. Furthermore, as eq 31 is simply a different representation of eq 3, it may be broken down as follows into contributions from the three different reactions involved:

PA–E reaction

$$(d\alpha/dt)_1 = B(K_1 + BK_2\beta)(1 - \alpha)(1 - \beta)^2 \tag{38}$$

SA–E reaction

$$(d\alpha/dt)_2 = B(K_1 + BK_2\beta)(1 - \alpha)(1 - \beta)\beta \tag{39}$$

Etherification reaction

$$(d\alpha/dt)_3 = K_3(Y + \beta)^m(Z + \beta^2)^n(1 - \alpha) \tag{40}$$

It is sometimes assumed that the reaction can be approximately divided into two stages. At the beginning of the cure, the amine–epoxide reaction dominates and etherification is insignificant. Thus, K_3 can be set equal to zero. Equation 27 then reduces to $\alpha = B\beta$, and eq 25 reduces to eq 1, the Horie equation with $r = {}^1/_2$. Toward the end of the cure, the approximation can be made that all the amine groups have reacted and the hydroxyl concentration is constant. In this case $\beta \approx 1$ and eq 31 reduces to

$$d\alpha/dt = K_3(Y + 1)^m(Z + 1)^n(1 - \alpha) = K'_3(1 - \alpha) \tag{41}$$

In other words, at the end of the cure the reaction tends to become simply first order with respect to epoxide concentration. This approximate approach has been applied with some success to one commercial system.[14]

Conclusion

A new approach to modeling the cure of epoxy resins with primary amines has been developed. It is based on the model proposed by Horie but is extended to include the etherification reaction. The basic assumptions inherent in the model are (i) the epoxide–amine reactions are hydroxyl catalyzed; (ii) the secondary amine groups have the same reactivity with respect to epoxide as the primary amine groups; and (iii) the etherification reaction is first order with respect to epoxide concentration and may also involve hydroxyl groups, tertiary amine groups, or both. The model makes use of no empirical parameters and no noninteger reaction orders. The evolution of the reaction is described in terms of two variables, α and β. The first is the usual overall epoxide conversion. The second is a measure of the extent of the epoxide–amine reaction. Thus the two different reaction pathways can be followed quantitatively. The kinetic equations have been solved to obtain an analytical relationship between α and β. Although an explicit expression cannot be derived to relate $d\alpha/dt$ to α, both can be expressed in terms of β. Thus the exact relationship between the two can be calculated on a point-by-point basis for a given set of the three rate constants involved. The best values for the rate constants can be determined by calculating a curve of $d\alpha/dt$ versus α, comparing it to experimental data, and varying the rate constants until a suitable match is achieved. Once the rate constants are known, the curing process can be completely described, including the evolution of the different chemical species as a function of the degree of cure. The effect on the kinetics of a change in amine/epoxy ratio can also be predicted. Compared to previous models, this new approach has the important advantage of allowing an accurate description of the curing process over the whole range of cure, without introducing empirical parameters or making approximations such as separating the reaction into distinct regimes. Although developed for epoxy cured with primary amine, the model could be modified to cover the case of secondary or mixed amines. In the succeeding paper, the successful application of the model to a typical commercial product is described.

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