Statistical structural model for the build-up of epoxy–amine networks with simultaneous etherification

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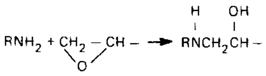
A statistical structural model is developed to describe a diepoxy–diamine cure, taking into account the possibility of simultaneous epoxy–hydroxy reaction (etherification). Expressions for the number- and weight-average molecular weights, gel conversion, sol fraction, mass fraction of pendant and elastically active network chains (EANC) and concentration of EANC are derived. The different reactivity of primary and secondary amine hydrogens is taken into account, but intramolecular reactions in the pregel stage are neglected. The model is applied to the cure of bisphenol A diglycidyl ether with diaminodiphenyl sulphone, where a previous kinetic analysis showed the presence of etherification. It is shown that, for stoichiometric formulations, etherification acts to decrease both the gel conversion and the concentration of EANC at full epoxy conversion. However, the elastic modulus of the material is not expected to change significantly. Instead, for formulations containing a 100% epoxy excess, the predicted elastic modulus at full epoxy conversion is 50% higher than that predicted for a stoichiometric mixture.

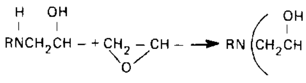
(Keywords: statistics; networks; epoxy; amine; etherification)

INTRODUCTION

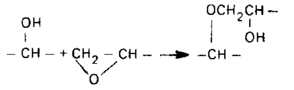
The reaction of epoxy compounds with primary amines takes place through the following paths[1]:



$$\mathrm{RNH_2} + \underset{\mathrm{O}}{\mathrm{CH_2{-}CH}}{-} \longrightarrow \mathrm{R}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{CH_2}\overset{\mathrm{OH}}{\mathrm{CH}}{-} \qquad (1)$$



$$\mathrm{R}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{CH_2}\overset{\mathrm{OH}}{\mathrm{CH}}{-} + \underset{\mathrm{O}}{\mathrm{CH_2{-}CH}}{-} \longrightarrow \mathrm{RN}\left(\mathrm{CH_2}\overset{\mathrm{OH}}{\mathrm{CH}}{-}\right)_2 \qquad (2)$$



$$-\overset{\mathrm{OH}}{\mathrm{CH}}- + \underset{\mathrm{O}}{\mathrm{CH_2{-}CH}}{-} \longrightarrow -\underset{}{\overset{\mathrm{OCH_2\overset{OH}{CH}-}}{\mathrm{CH}}}- \qquad (3)$$

A fourth possibility, namely the homopolymerization of epoxy groups, requires the presence of Lewis bases (i.e. tertiary amines), inorganic bases (i.e. NaOH) or Lewis acid catalysts (i.e. F_3B complexed with an amine)[2,3]. As the tertiary amine arising from step (2) is usually sterically hindered, its catalytic effect towards the homopolymerization reaction will not be significant[1]. Note, however, that step (3) acts as a polyaddition reaction without termination, and, in this sense, it is structurally equivalent to the epoxide homopolymerization.

The relevance of step (3) with respect to the two other reactions depends on the nature of the diamine, the epoxy/amine ratio, and the reaction temperature. There is plenty of experimental evidence indicating that, for stoichiometric mixtures of epoxy resins with aliphatic diamines, step (3) may be neglected[1,4–8]. However, for aromatic diamines this may no longer be the case owing to the low reactivity of the secondary amine with respect to the primary one[9], and the higher curing temperatures. Evidence of the epoxy–hydroxy reaction has been presented for the curing of tetraglycidyl 4,4′-diaminodiphenyl methane (TGDDM) with diaminodiphenyl sulphone (DDS)[10–13], and the curing of bisphenol A diglycidyl ether (BADGE) with DDS[14]. For the last system, it was shown that step (3) was significant at temperatures higher than 150°C and at high reaction extents, when the primary amine had been sufficiently depleted[14]. Obviously, working with a stoichiometric excess of the epoxy compound enhances the possibility of etherification. This excess of epoxy groups is usually prescribed in formulations of commercial interest based on TGDDM and DDS[15]. Then, the analysis of the influence of etherification on parameters characterizing the network structure is of practical interest.

A rigorous statistical analysis of the curing of epoxy resins with amine curing agents has been presented by Dušek *et al.*[7], with the aid of the theory of cascade processes. The possibility of etherification was neglected, but the different reactivity of hydrogen atoms in the primary and secondary amino groups was taken into account.

Burchard *et al.*[16,17] analysed the reaction between BADGE and bisphenol A taking into account the possibility of chain branching caused by the addition of epoxide to a secondary hydroxyl group formed in the chain lengthening step. Under mild conditions, i.e. at 100°C, bisphenol A reacts more rapidly than the secondary OH group. Thus, etherification (branching) takes place when nearly all phenolic hydroxyl groups have been consumed. At higher temperatures, i.e. at 150°C, extensive etherification can take place, an effect

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similar to the one reported for the BADGE–DDS reaction[14]. A statistical method based on the theory of cascade processes was used to derive concise analytic equations for the weight- (M_w) and number-average (M_n) molecular weights as functions of the extents of reaction of phenolic and epoxy groups and the branching probability (ratio of rate constants for etherification and chain lengthening).

Bokare and Gandhi[18] studied the effect of the simultaneous etherification reaction on the curing of epoxides with amines, i.e. the same system represented by equations (1) to (3). The discussion was restricted to the effect of epoxy/amine stoichiometric ratios and rate constant ratios on the weight-average molecular weight and the gelation condition. The analysis was based on a combination of a kinetic model accounting for the generation of clusters of epoxy groups and the expectation theory developed by Macosko and Miller[19]. Owing to the relatively low values assigned to the etherification rate constant, its effect was significant only when an initial excess of epoxy over amine groups was assumed. In general, the epoxy conversion at gelation decreased when the etherification rate increased, i.e. step (3) accelerates gelation of the system. Recently, Dušek[20] analysed the network build-up by the polyetherification of a diepoxide released by hydroxyl groups formed in the primary reaction with a diamine. The discussion was based on a kinetic model taking into account the epoxy clusters generated in the polyaddition reaction, combined with a statistical (cascade) method. Essentially this approach is the same as the one used by Bokare and Gandhi[18]. Although the model may be applied to general routine calculations of statistical parameters on pregel and postgel stages, only the effect of the etherification reaction on the gelation condition was analysed. A comparison of this model with the cascade substitution method based on diamine and diepoxide units is provided. The most significant result is the large deviation of both approaches and, therefore, the necessity of using a statistical method from kinetically generated epoxy–amine clusters.

The aim of the present paper is:

(a) to introduce a statistical structural model (SSM) based on a combination of a kinetic scheme accounting for the evolution of all possible fragments that may be generated from the network structure, together with a simple expectation theory (this approach has been previously used for the build-up of phenolic resin networks[21,22]);

(b) to generate statistical parameters both in the pregel and postgel stages of the complex polymerization reaction; and

(c) to illustrate the approach by applying it to an actual system (BADGE–DDS), where information on the different kinetic parameters, including the etherification reaction, is available[14].

A comparison among different approaches to generate statistical parameters ((i) statistics applied to kinetically generated *clusters*, (ii) statistics applied to kinetically generated *fragments* (SSM), and (iii) statistics applied to initial molecules using probability generating functions) will be discussed in another paper. We may, however, anticipate that predictions from (i) and (ii) are very close for the case of the postetherification of excess epoxy groups occurring after completion of the epoxy–amine reaction.

STATISTICAL STRUCTURAL MODEL (SSM)

Figure 1 shows the different structural elements present during the cure of the epoxy resin. Implicit in this notation is the fact that both epoxy groups of the same diepoxide molecule, and both amine groups of the same diamine molecule, have independent reactivities. Different structural fragments that may be distinguished as the cure proceeds are shown in *Figure 2*. Note that arrows are joined to arrows, segments to segments, and (+) asterisks to (−) asterisks.

Fragments E8 are part of a diepoxide molecule, i.e. a BADGE molecule containing OH groups. This fragmentation of the epoxy oligomers implicitly assumes an initial most probable distribution. In reality, the distribution may be arbitrary depending on the conditions of preparation.

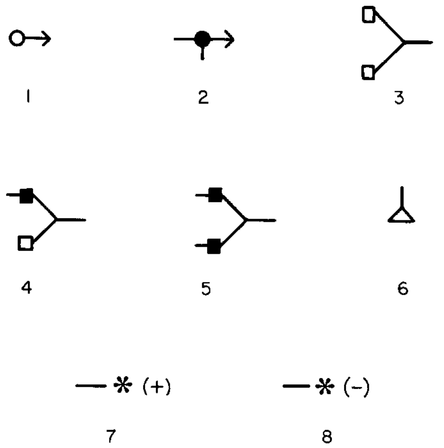

Figure 1 The various structural elements present during the cure of the epoxy resin: 1, unreacted epoxy; 2, reacted epoxy; 3, unreacted amine; 4, partially reacted amine; 5, completely reacted amine; 6, hydroxy group; 7 and 8, half-linkages that are joined between themselves, i.e. + with −

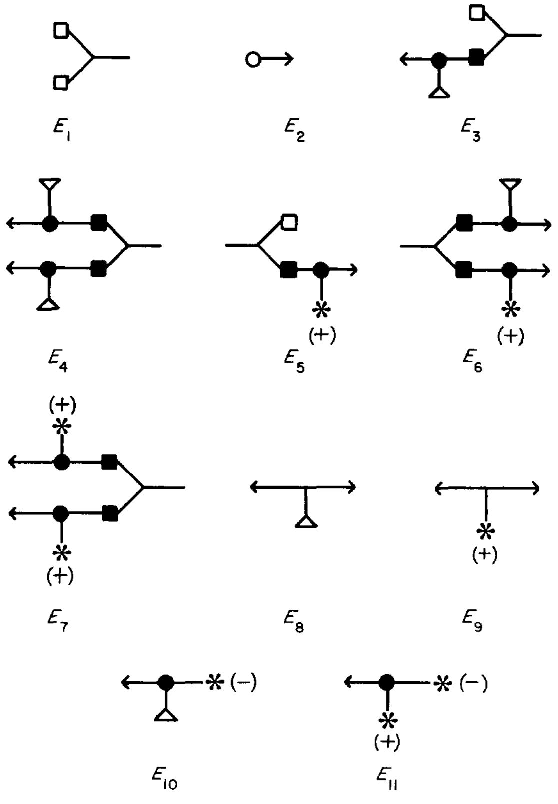

Figure 2 Structural fragments present during the cure of the epoxy resin

In terms of structural fragments, the reaction scheme may be written as

$$E_2+E_1\rightarrow E_3 \tag{4}$$

$$E_2+E_3\rightarrow E_5+E_{10} \tag{5}$$

$$E_2+E_3\rightarrow E_4 \tag{6}$$

$$E_2+E_4\rightarrow E_6+E_{10} \tag{7}$$

$$E_2+E_5\rightarrow E_6 \tag{8}$$

$$E_2+E_6\rightarrow E_7+E_{10} \tag{9}$$

$$E_2+E_8\rightarrow E_9+E_{10} \tag{10}$$

$$E_2+E_{10}\rightarrow E_{10}+E_{11} \tag{11}$$

Masses of the structural fragments will be denoted by M_1 to M_{11}.

The stoichiometric ratio of amine/epoxy equivalents is given by

$$r=2(E_1)_0/(E_2)_0 \tag{12}$$

The conversion of epoxy groups may be written as

$$x_e=(E_3+2E_4+E_5+2E_6+2E_7+E_{10}+E_{11})/(E_2)_0 \tag{13}$$

Knowledge of the kinetics of reactions (4) to (11) is necessary to find the evolution of the different fragments as a function of conversion. This will be discussed in the following section.

Pregel parameters

Assuming that no cyclization reaction takes place in the pregel stage, the number-average molecular weight may be calculated as follows:

$$M_n=(\text{total mass})/(\text{number of moles}) \tag{14}$$

$$\text{total mass}=(E_2)_0[M_2+M_1r/2+M_8(E_8)_0/(E_2)_0] \tag{15}$$

$$\text{number of moles}=(E_2)_0(0.5+0.25r-x_e) \tag{16}$$

Equation (16) assumes that, each time an epoxy reacts, the number of molecules diminishes in one unit (no intramolecular reactions). By substituting (15) and (16) into (14), we get

$$M_n=[M_2+M_1r/2+M_8(E_8)_0/(E_2)_0]/(0.5+0.25r-x_e) \tag{17}$$

Thus, a unique M_n vs. x_e function is obtained once the type of reactants and the stoichiometric ratio are selected.

In order to calculate the weight-average molecular weight, M_w, let us define: Y = average weight hanging from an arrow (→), Z = average weight hanging from a segment (—), W_P = average weight hanging from a linkage —*(+), W_N = average weight hanging from a linkage —*(−). Conceptually, the idea is that we are fishing with a certain hook, i.e. an arrow, and want to know the weight, i.e. Y, of the fish that will be obtained. This is calculated as follows:

$$\begin{aligned}Y=\textstyle\sum_{\text{fragments}}&\text{(fraction of total arrows associated with a particular fragment)}\\&\times\text{(average weight hanging from the fragment already linked by an arrow)}\end{aligned} \tag{18}$$

Then

$$\begin{aligned}Y=[&E_2M_2+E_3(M_3+Z)+2E_4(M_4+Y+Z)\\&+E_5(M_5+W_P+Z)+2E_6(M_6+Y+Z+W_P)\\&+2E_7(M_7+Y+Z+2W_P)+2E_8(M_8+Y)+2E_9(M_9\\&+Y+W_P)+E_{10}(M_{10}+W_N)+E_{11}(M_{11}+W_P\\&+W_N)]/[(E_2)_0(1+2(E_8)_0/(E_2)_0)]\end{aligned} \tag{19}$$

Again, implicit in the calculation of Y, is the fact that cyclization reactions are considered negligible.

Similarly, the other average weights are calculated as

$$\begin{aligned}Z=[&E_1M_1+E_3(M_3+Y)+E_4(M_4+2Y)\\&+E_5(M_5+Y+W_P)+E_6(M_6+2Y+W_P)\\&+E_7(M_7+2Y+2W_P)]/[(E_2)_0r/2]\}\end{aligned} \tag{20}$$

$$W_P=[E_{10}(M_{10}+Y)+E_{11}(M_{11}+Y+W_P)]/(E_{10}+E_{11}) \tag{21}$$

$$\begin{aligned}W_N=[&E_5(M_5+Y+Z)+E_6(M_6+2Y+Z)\\&+2E_7(M_7+2Y+Z+W_P)+E_9(M_9+2Y)\\&+E_{11}(M_{11}+Y+W_N)]/(E_{10}+E_{11})\end{aligned} \tag{22}$$

In equation (22), the fact that the total number of positive asterisks is equal to the total number of negative asterisks $=E_{10}+E_{11}$, has been taken into account.

The system of four equations (19) to (22), in four unknowns (Y,Z,W_P,W_N), may be solved as a function of the reaction extent. The average weight hanging from each fragment is written as:

$$\begin{aligned}M_{T(1)}&=M_1+Z\\M_{T(2)}&=M_2+Y\\M_{T(3)}&=M_3+Y+Z\\M_{T(4)}&=M_4+2Y+Z\\M_{T(5)}&=M_5+Y+Z+W_P\\M_{T(6)}&=M_6+2Y+Z+W_P\\M_{T(7)}&=M_7+2Y+Z+2W_P\\M_{T(8)}&=M_8+2Y\\M_{T(9)}&=M_9+2Y+W_P\\M_{T(10)}&=M_{10}+Y+W_N\\M_{T(11)}&=M_{11}+Y+W_P+W_N\end{aligned}$$

The mass fraction of each of the structural fragments, $W(I)$ $(I=1$ to $11)$, is given by

$$W(I)=E_IM_I/\{(E_2)_0[M_2+M_1r/2+M_8(E_8)_0/(E_2)_0]\} \tag{23}$$

The weight-average molecular weight is defined as

$$M_w=\textstyle\sum_I W(I)M_{T(I)} \tag{24}$$

The gelation conversion, x_{gel}, is the reaction extent at which $M_w\rightarrow\infty$. This condition is verified when $(Y,Z,W_P,W_N)\rightarrow\infty$. Introducing equations (21) and (22) into equations (19) and (20), it may be shown that both Y and Z (and consequently W_P and W_N) become infinite when

$$\begin{aligned}&(E_2)_0(r/2)\{(E_2)_0[1+2(E_8)_0/(E_2)_0]\\&\quad-2[E_4+E_6+E_7+E_8+E_9+(1+E_{11}/E_{10})\\&\quad\times(E_5+2E_6+E_7(5+E_{11}/E_{10})+2E_9+E_{11})]\}\\&\quad=[E_3+2E_4+E_6+(2+E_{11}/E_{10})(E_5+E_6+2E_7)]^2\end{aligned}\tag{25}$$

It is interesting to consider particular cases of the general gelation condition given by equation (25). For example, if etherification is neglected, the system may be described by fragments E_1 to E_4 (and E_8 may be regarded as an inert fragment included in E_2 and in the associated mass M_2). Then, (25) reduces to

$$(E_2)_0(r/2)[(E_2)_0-2E_4]=(E_3+2E_4)^2\tag{26}$$

Also, from (13),

$$x_e=(E_3+2E_4)/(E_2)_0\tag{27}$$

Substituting equation (27) into (26) and rearranging, we get

$$x_e^2=(r/2)[1-2E_4/(E_2)_0]\tag{28}$$

If we further assume that the polymerization is ideal, i.e. there are no substitution effects, the fraction of bireacted amine groups is given by

$$E_4/(E_1)_0=x_a^2\tag{29}$$

where the conversion of amine hydrogens, x_a, is related to x_e through

$$x_e=rx_a\tag{30}$$

Substituting (12), (29) and (30) into (28), and rearranging, gives the result

$$x_e=(r/3)^{1/2}\tag{31}$$

which is the Flory–Stockmayer prediction for an ideal A_4+B_2 polymerization[7].

Other interesting limits of equation (28) are cases with extreme substitution effects. If we call $N=k_2/k_1$ the reactivity ratio of a secondary to a primary amine hydrogen, the two limiting cases of $N=0$ and $N\to\infty$ may be analysed. For $N\to\infty$, $E_3\to 0$, because once a primary amine hydrogen reacts, the generated secondary amine is immediately reacted. Then, from (27)

$$x_e=2E_4/(E_2)_0\tag{32}$$

Substituting (32) into (28) and solving, we get

$$x_e=0.5(0.25r^2+2r)^{1/2}-0.25r\tag{33}$$

For a stoichiometric system, i.e. $r=1$, (33) reduces to

$$x_e=0.5\tag{34}$$

which agrees with the result reported by Dušek *et al.*[7], using the theory of cascade processes.

On the other hand, for $N=0$ the system will gel after all E_1 has been converted to E_3. From this time on, it is verified that

$$E_4=(E_1)_0-E_3\tag{35}$$

Substituting (35) into (27) and solving the system of equations (27) and (28), we obtain

$$x_e=\{(r/2)[1+2r-(3r^2+2r)^{1/2}]\}^{1/2}\tag{36}$$

For $r=1$, (36) leads to

$$x_e=0.618\tag{37}$$

which, again, agrees with the result found by Dušek *et al.*[7]

Thus, it has been proved that the general gelation condition, equation (25), reduces to known particular cases. This also assures us of the reliability of the SSM and its suitability to deal with complex polymerization schemes.

Postgel parameters

In order to derive postgel properties, extinction probabilities of different chains must be defined. Let us call R, S, T_P and T_N the probability of finding a finite chain leaving a particular fragment from an arrow (→), a segment (—), a linkage $-*(+)$ and a linkage $-*(-)$, respectively. Now we fish with a certain hook, i.e. an arrow, and want to know the probability, i.e. R, of getting out a finite species. This is calculated as follows:

$$\begin{aligned}R=&\textstyle\sum_{\text{fragments}}\text{(fraction of total arrows associated with a particular fragment)}\\&\times\text{(probability that all branches leaving from the fragment, already linked by an arrow, are finite)}\end{aligned}\tag{38}$$

Then

$$\begin{aligned}R=&(E_2+E_3S+2E_4RS+E_5ST_P+2E_6RST_P\\&+2E_7RST_P^2+2E_8R+2E_9RT_P\\&+E_{10}T_N+E_{11}T_pT_N)/\{(E_2)_0[1+2(E_8)_0/(E_2)_0]\}\end{aligned}\tag{39}$$

Similarly, the other extinction probabilities are given by

$$\begin{aligned}S=&(E_1+E_3R+E_4R^2+E_5RT_P+E_6R^2T_P+E_7R^2T_P^2)/\\&[(E_2)_0r/2]\end{aligned}\tag{40}$$

$$T_P=(E_{10}R+E_{11}RT_P)/(E_{10}+E_{11})\tag{41}$$

$$\begin{aligned}T_N=&(E_5RS+E_6R^2S+2E_7R^2ST_P+E_9R^2+E_{11}RT_N)/\\&(E_{10}+E_{11})\end{aligned}\tag{42}$$

Solving the system of four equations in four unknowns, the values of R, S, T_P and T_N may be obtained as a function of the reaction extent. This is performed by rearranging (40) to (42) to express S, T_P and T_N as a function of R. The results are substituted into (39) and R is found with a suitable numerical algorithm, i.e. Newton's method.

The sol fraction may be calculated as

$$\begin{aligned}w_s=&W(1)S+W(2)R+W(3)RS+W(4)R^2S+W(5)RST_P\\&+W(6)R^2ST_P+W(7)R^2ST_P^2+W(8)R^2+W(9)R^2T_P\\&+W(10)RT_N+W(11)RT_PT_N\end{aligned}\tag{43}$$

A structural fragment is part of a pendant chain if only one of its arms is joined to the gel. Thus, mass fraction of pendant chains is given by

$$\begin{aligned} w_p = {} & W(1)(1-S)+W(2)(1-R)+W(3)[(1-R)S \\ & +(1-S)R]+W(4)[2(1-R)RS+(1-S)R^2] \\ & +W(5)[(1-S)RT_P+(1-R)ST_P+(1-T_P)RS] \\ & +W(6)[2(1-R)RST_P+(1-S)R^2T_P+(1-T_P)R^2S] \\ & +W(7)[2(1-R)RST_P^2+2(1-T_P)T_PSR^2+(1-S)R^2T_P^2] \\ & +W(8)2(1-R)R+W(9)[2(1-R)RT_P+(1-T_P)R^2] \\ & +W(10)[(1-R)T_N+(1-T_N)R] \\ & +W(11)[(1-R)T_PT_N+(1-T_P)RT_N+(1-T_N)RT_P] \end{aligned} \quad (44)$$

The mass fraction of material pertaining to elastically active network chains results from

$$w_e = 1 - w_s - w_p \quad (45)$$

The concentration of crosslinking units per initial epoxy equivalent, with three branches going to the gel, X_3, may be calculated as:

$$\begin{aligned} X_3 = {} & \{E_4(1-R)^2(1-S)+E_5(1-R)(1-S)(1-T_P) \\ & +E_6[2(1-R)R(1-S)(1-T_P)+(1-R)^2(1-S)T_P \\ & +(1-R)^2(1-T_P)S]+E_7[(1-R)^2(1-S)T_P^2 \\ & +4(1-R)R(1-T_P)T_P(1-S) \\ & +2(1-R)R^2(1-T_P)^2S \\ & +2(1-T_P)T_P(1-R)^2S+(1-S)(1-T_P)^2R^2] \\ & +E_9(1-R)^2(1-T_P)+E_{11}(1-R)(1-T_P)(1-T_N)\}/ \\ & (E_2)_0 \end{aligned} \quad (46)$$

Similarly,

$$\begin{aligned} X_4 = {} & \{E_6(1-R)^2(1-S)(1-T_P)+E_7[(1-R)^2(1-T_P)^2S \\ & +2(1-R)^2(1-S)(1-T_P)T_P \\ & +2(1-T_P)^2(1-S)(1-R)R]\}/(E_2)_0 \end{aligned} \quad (47)$$

$$X_5 = \{E_7(1-R)^2(1-T_P)^2(1-S)\}/(E_2)_0 \quad (48)$$

The concentration of elastically active network chains, per initial epoxy equivalent, is given by

$$\mathrm{EANC} = (3X_3+4X_4+5X_5)/2 \quad (49)$$

Note that, as half of the diepoxides or diamines are considered as crosslinks, it is implicitly assumed that diamine or diepoxide units can act as EANCs (this is convenient due to the high crosslinking density of the networks).

KINETIC SCHEME

The kinetics of the formation of epoxy–amine networks with simultaneous etherification has been reported elsewhere[14]. Similarly to steps (1) and (2), step (3) may take place both by a noncatalytic path and by a reaction catalysed by OH groups. The rate of disappearance of epoxy groups may be written as:

$$\begin{aligned} -\mathrm{d}E_2/\mathrm{d}t = {} & E_2[k'_1 2E_1+k_1(\mathrm{OH})2E_1+k'_2(E_3+E_5) \\ & +k_2(\mathrm{OH})(E_3+E_5)+k'_3(\mathrm{OH})+k_3(\mathrm{OH})^2] \end{aligned} \quad (50)$$

where k'_1, k'_2 and k'_3 are noncatalytic specific rate constants, while k_1, k_2 and k_3 are the specific rate constants for the reactions catalysed by OH groups $(E_3+2E_4+E_6+E_8+E_{10})$. Subscripts 1, 2 and 3 correspond to the three reaction paths described by equations (1) to (3).

Let us define:

$$N = k'_2/k'_1 = k_2/k_1$$

(reactivity ratio of secondary and primary amine hydrogens; for a system without substitution effects, $N=1$)

$$L = k'_3/k'_1 = k_3/k_1$$

(ratio of the etherification reaction with respect to the addition to a primary amine)

$$M = k'_1/k_1(E_2)_0 = k'_2/k_2(E_2)_0 = k'_3/k_3(E_2)_0$$

(ratio of the noncatalytic to the catalytic reaction)

$$E_I^* = E_I/(E_2)_0 \qquad (I = 1 \text{ to } 11)$$

(dimensionless concentration)

$$(\mathrm{OH})^* = E_3^* + 2E_4^* + E_6^* + E_8^* + E_{10}^*$$

$$E^* = E_2^*[M + (\mathrm{OH})^*]$$

$$t^* = k_1(E_2)_0^2 t$$

(dimensionless time).

Then, (50) may be written as

$$-\mathrm{d}E_2^*/\mathrm{d}t^* = E^*[2E_1^* + N(E_3^* + E_5^*) + L(\mathrm{OH})^*] \quad (51)$$

Similarly, the rates of variation of the other structural fragments are given by:

$$-\mathrm{d}E_1^*/\mathrm{d}t^* = E^* 2E_1^* \quad (52)$$

$$\mathrm{d}E_3^*/\mathrm{d}t^* = E^*[2E_1^* - (N+L)E_3^*] \quad (53)$$

$$\mathrm{d}E_4^*/\mathrm{d}t^* = E^*(NE_3^* - 2LE_4^*) \quad (54)$$

$$\mathrm{d}E_5^*/\mathrm{d}t^* = E^*(LE_3^* - NE_5^*) \quad (55)$$

$$\mathrm{d}E_6^*/\mathrm{d}t^* = E^*(2LE_4^* + NE_5^* - LE_6^*) \quad (56)$$

$$\mathrm{d}E_7^*/dt^* = LE_6^* E^* \quad (57)$$

$$-\mathrm{d}E_8^*/\mathrm{d}t^* = LE_8^* E^* \quad (58)$$

$$\mathrm{d}E_9^*/\mathrm{d}t^* = LE_8^* E^* \quad (59)$$

$$\mathrm{d}E_{10}^*/\mathrm{d}t^* = E^* L(E_3^* + 2E_4^* + E_6^* + E_8^*) \quad (60)$$

$$\mathrm{d}E_{11}^*/\mathrm{d}t^* = E^* L E_{10}^* \quad (61)$$

The system of equations (51) to (61) is solved using a fourth-order Runge–Kutta method. The concentration of the different fragments, E_1^* to E_{11}^* is expressed as a function of the epoxy conversion, x_e, given by (13).

SELECTED SYSTEM

In order to illustrate the statistical calculations, the curing of a commercial BADGE (Araldit GY 250, Ciba-Geigy) with DDS (HT 976, Ciba-Geigy) will be discussed. The system is characterized by the following parameters[14]: $(E_8)_0/(E_2)_0=0.061$; $M_1=124$; $M_2=170$, $M_3=294$, $M_4=464$, $M_5=293$, $M_6=463$, $M_7=462$, $M_8=284$, $M_9=283$, $M_{10}=171$, $M_{11}=170$ (all M_I are expressed in g mol^{-1}); $N=0.4$ (determined from the critical gelation ratio of formulations cured with an amine excess); $L=0.14\pm0.03$ (a value of $L=0$ will also be taken for comparison purposes). Two different stoichiometric ratios will be selected: $r=1$ (stoichiometric mixture), and $r=0.5$ (100% epoxy excess). For the first one, $M=5.76\times10^{-2}$ at 200°C (temperature higher than the glass transition temperature at full conversion), whilst for the mixture with an epoxy excess $M=5.01\times10^{-2}$ at 200°C.

RESULTS AND DISCUSSION

In order to obtain an overall check of the SSM, an ideal A_4+B_2 system ($L=0$, $N=1$) was first solved. Statistical parameters in the pregel and postgel stages were compared with results reported in the literature[19,23], and showed complete agreement. Having confirmed the correct reduction to the ideal case, the SSM was then solved for the epoxy–amine cure with simultaneous etherification.

Figures 3 and *4* show the concentration of different fragments as a function of the epoxy conversion. Stoichiometric mixtures without etherification ($r=1$, $L=0$) show that the primary amine is completely converted to tertiary amine at the end of the polymerization, while the secondary amine goes through a maximum. When etherification is allowed ($r=1$, $L=0.14$), the secondary amine (E_3 and E_5) is still present at complete conversion, and fragments E_6 and E_{10} appear in significant concentrations. If the system is formulated with a 100% epoxy excess ($r=0.5$, $L=0.14$), the secondary amine is almost depleted at high epoxy conversions, while fragments like E_6, E_7, E_{10} and E_{11}, arising from the etherification reaction, show a significant concentration increase.

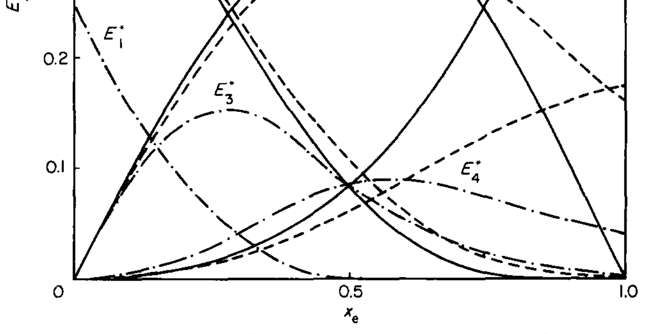

Figure 3 Concentration of different amines as a function of the epoxy conversion: (——) $r=1$, $L=0$; (– – –) $r=1$, $L=0.14$; (–·–·–) $r=0.5$, $L=0.14$

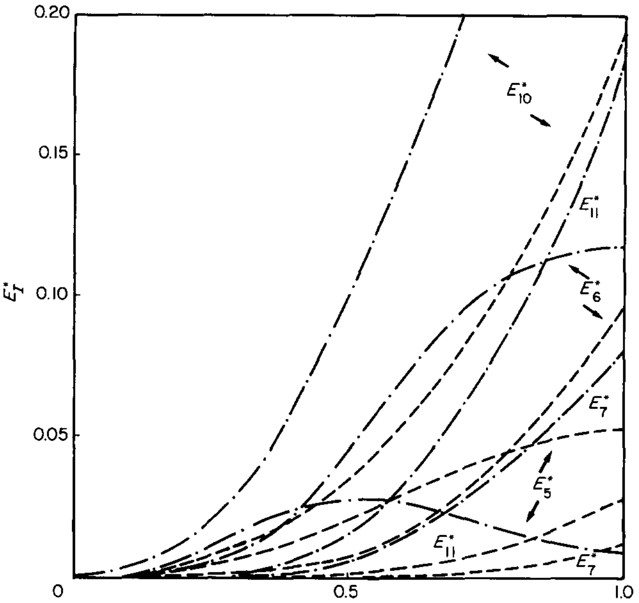

Figure 4 Concentration of different fragments as a function of the epoxy conversion: (– – –) $r=1$, $L=0.14$; (–·–·–) $r=0.5$, $L=0.14$

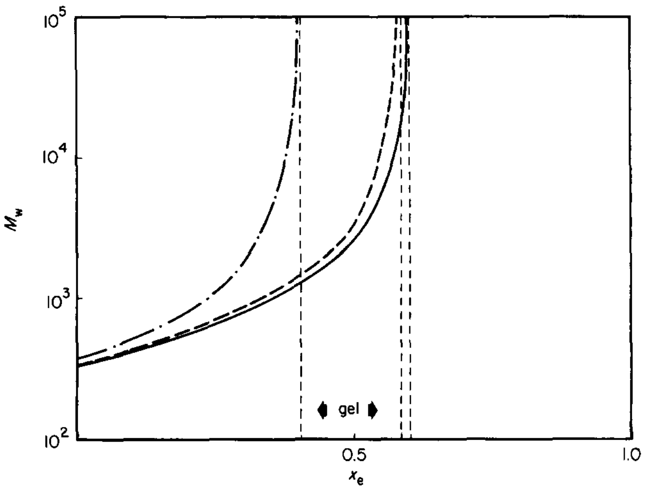

Figure 5 Weight-average molecular weight *versus* the epoxy conversion: (——) $r=1$, $L=0$; (– – –) $r=1$, $L=0.14$; (–·–·–) $r=0.5$, $L=0.14$

The evolution of the weight-average molecular weight, M_w, with the epoxy conversion is shown in *Figure 5*. Etherification leads to earlier gelation, particularly when an epoxy excess is used. This is due to the extra branching generated in the network structure.

Figure 6 shows the evolution of sol fraction, pendant chains and elastic material for stoichiometric ($r=1$) and nonstoichiometric mixtures ($r=0.5$), when the etherification reaction contributes to the cure ($L=0.14$). The more significant is etherification, i.e. for $r=0.5$, the less pronounced are decrease of sol fraction and the amount of pendant chains. Thus, while this mechanism leads to high-functionality branching points, it also retards the incorporation of finite molecules into the gel as well as the change of pendant into elastically active chains. This results from the fact that one of the coreactants, i.e. OH groups, not only is not depleted but, instead, increases its concentration throughout the polymerization. These OH functionalities may pertain to elastic, pendant or soluble material, and they compete among them for the reaction with epoxy groups, i.e. the probability of producing intramolecular cyclization in the gel is increased.

Figure 7 shows the evolution of f-functional crosslinking junctions ($f=3$ to 5) during network formation. Working with an epoxy excess leads to a higher concentration of 4- and 5-functional crosslinking units (fraction of E_6 and E_7 with all branches going to the gel). The EANC concentration is shown in *Figure 8* as a function of the reaction extent. For stoichiometric mixtures the etherification reaction leads to an early increase of the EANC; however, at the end of the polymerization the system without etherification shows a higher concentration of elastically active network chains. This is the result of the presence of chain extenders, i.e. fragments E_3 and E_{10}, in the system with etherification. When the epoxy–amine is the only reaction, these chain extenders are replaced by 3-functional crosslinking units, i.e. the fragment E_4. On the other hand, a system with 100% epoxy excess ($r=0.5$) shows a higher EANC concentration at the end of the polymerization (the calculation is based on an initial-epoxy-equivalent basis; the difference is slightly enhanced on a mass or volume basis).

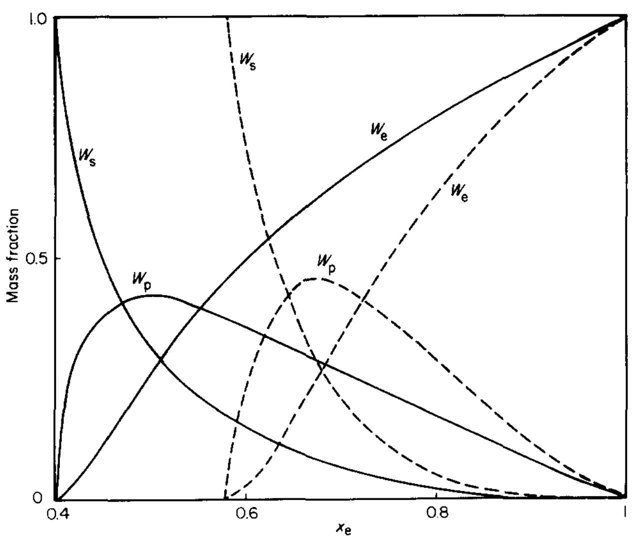

Figure 6 Mass fraction of soluble material, w_s, pendant chains, w_p, and elastically active network chains, w_e, *versus* the epoxy conversion: (– – –) $r=1$, $L=0.14$; (———) $r=0.5$, $L=0.14$

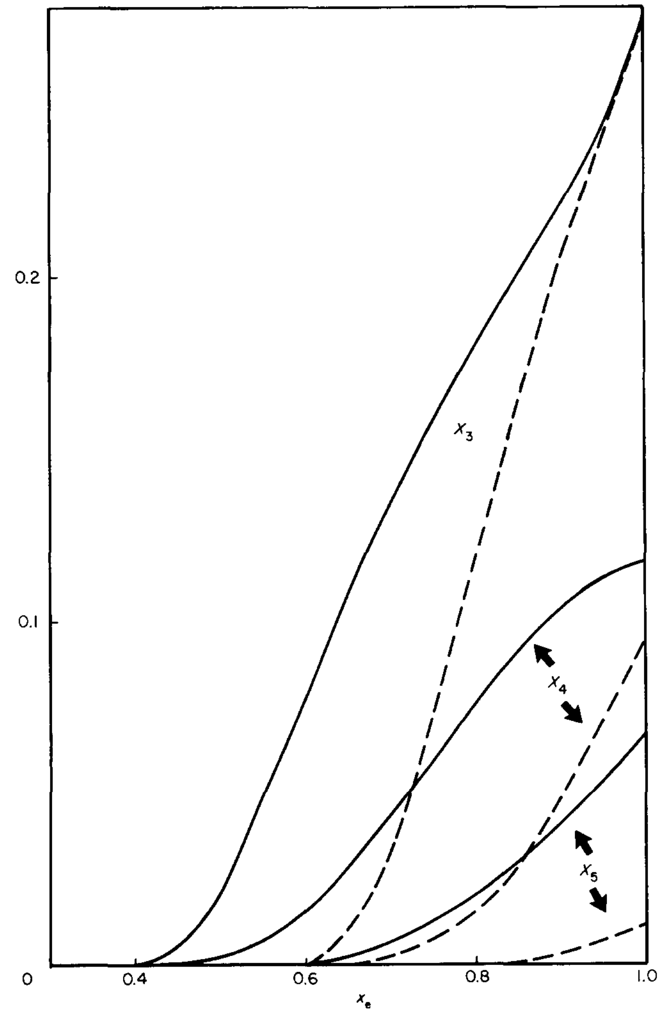

Figure 7 Concentration of f-functional crosslinking junctions ($f=3$ to 5), per initial epoxy equivalent, *versus* the epoxy conversion: (– – –) $r=1$, $L=0.14$; (———) $r=0.5$, $L=0.14$

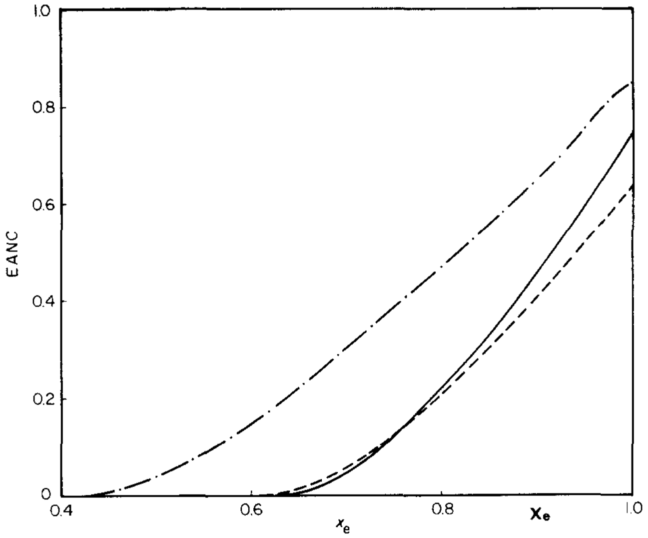

Figure 8 Concentration of elastically active network chains, per initial epoxy equivalent, as a function of the epoxy conversion: (———) $r=1$, $L=0$; (– – –) $r=1$, $L=0.14$; (–·–·–) $r=0.5$; $L=0.14$

The elastic modulus of the material is proportional to the EANC concentration. If a nonaffine deformation is assumed, i.e. a phantom network deformation, the weight factor $(f-2)/f$ has to be included in the calculation. Then, a reduced elastic modulus may be defined as

$$E_c^* = \sum_{f=3}^{5} [(f-2)/f](f/2)X_f = \sum_{f=3}^{5} (f/2-1)X_f \qquad (62)$$

Figure 9 shows the evolution of the reduced elastic modulus as a function of the epoxy conversion. At the end of the polymerization the system with 100% epoxy excess reaches an elastic modulus 50% greater than that of stoichiometric systems. Note that in this last case ($r=1$), the elastic modulus is practically unaltered by the etherification reaction, owing to the presence of a compensation effect between the higher concentration of EANC and the lower functionality of crosslinking junctions. For $L=0$, the final value, $E_c^*=0.25$, arises from the fact that $X_3=E_4^*=0.5$ (*Figure 3*).

CONCLUSIONS

A statistical structural model (SSM) was developed to describe a diepoxy–diamine cure, taking into account the possibility of different reactivity of primary and secondary amine hydrogens, as well as a simultaneous epoxy–

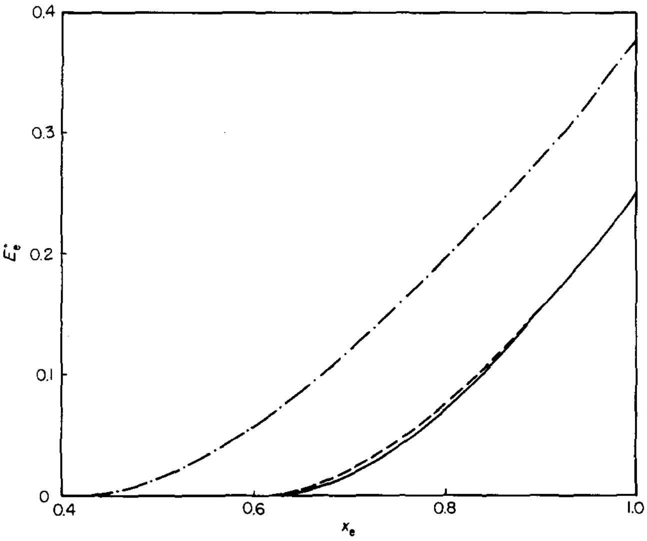

Figure 9 Reduced elastic modulus as a function of the epoxy conversion: (———) $r=1$, $L=0$; (– – –) $r=1$, $L=0.14$; (–·–·–) $r=0.5$, $L=0.14$

hydroxy reaction (etherification). Expressions for pregel and postgel parameters were derived by neglecting intramolecular reactions in the pregel stage. The resulting gelation condition was shown to reduce correctly to cases where the etherification reaction was not considered in the analysis. A comparison of this approach with a statistical method applied to kinetically generated clusters[18,20] will be discussed in another paper.

A BADGE–DDS system was selected for the simulation because a kinetic characterization was available[14]. For stoichiometric mixtures, the presence of a simultaneous epoxy–hydroxy reaction leads to early gelation but a lower final concentration of EANC. The decrease in gel conversion is the result of extra branching associated with etherification. The lower final EANC concentration results from the fact that some fragments end as chain extenders, instead of being converted into crosslinking junctions. However, owing to the compensation produced by the fact that the higher EANC concentration is associated with a lower functionality of crosslinking units, no significant change in the elastic modulus can be expected as a result of etherification. On the other hand, for formulations containing a 100% epoxy excess, the predicted elastic modulus at full epoxy conversion is 50% higher than that predicted for a stoichiometric system. Here, etherification increases both the EANC concentration and the average functionality of crosslinking junctions.

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