Influence of prepolymerization on gelation of diepoxide–diamine systems

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The polymerization of diepoxide-diamine is simulated using a two-stage procedure. In the first stage a convenient epoxy or amine excess is used to prepare a liquid prepolymer at complete conversion, which is then cured in a second step by balancing stoichiometry. The possibility of a secondary addition of the excess monomer is also considered. The extent of reaction leading to gelation in the second stage is obtained analytically for ideal systems and numerically when substitution effects in the amine hydrogens are taken into account. By selection of an appropriate initial stoichiometry, the gel conversion in the second stage may be considerably reduced when compared to the typical one-stage stoichiometric system ($p_{gel} \simeq 0.6$). This may have practical applications for reducing residence times in heated moulds or to freeze a phase separation process produced in the first stage of the polymerization.

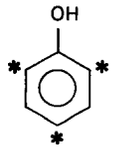
(Keywords: two-stage polymerization; epoxy-amine polymerization; gelation; statistics; prepolymers)

INTRODUCTION

The use of prepolymerization techniques is relatively widespread in the processing of thermosetting polymers. It consists essentially in carrying out the polymerization in two steps. In the first step, a convenient excess of one of the monomers is used, such that gelation is not attained even at full conversion of the monomer in deficit. In the second step, stoichiometry is balanced and polymerization is carried out to completion.

Some advantages of using a prepolymerization technique are: decrease in temperature rise during cure; advance in the gel point and consequent decrease in the cycle time for demoulding; decrease in the vapour pressure when using volatile monomers; decrease in the shrinkage of the part; possibility of producing a phase separation during the first stage for a rubber-modified thermoset formulation, such that the morphology remains frozen during the second stage. Possible disadvantages of the two-step operation are: increased costs through the need of prepolymerization installations; increase in the viscosity of one of the streams.

Possibly the oldest system using a two-step polymerization is that of phenolic resins of the novolac type. In this case, phenol (in excess) is polymerized with formaldehyde (in deficit), in an acid medium, to give a novolac. This in turn is cured with a second amount of formaldehyde and a base, in a second step, to give the final product (bakelite). Phenol is a trifunctional monomer:



(*o*, *o'* and *p* positions)

whereas formaldehyde is a bifunctional monomer: HO—CH_2—OH (represented as methylene glycol in a water solution).

For ideal polymerization (equal reactivity, absence of substitution effects and intramolecular cycles in finite species) of an $A_f + B_g$ system, the critical stoichiometric ratio when working with a deficit of A_f, is given by[1–4]:

$$r_c = (fA_f/gB_g)|_c = 1/[(f-1)(g-1)] \quad (1)$$

where f and g are the functionalities (number of reactive sites) of both monomers.

Therefore, if the phenol (Ph) – formaldehyde (F) polymerization is regarded as an ideal reaction, the condition to avoid gelation in the first step is $r < r_c$, or in terms of molar ratios:

$$(F/Ph) < 0.75 \quad \text{(ideal)} \quad (2)$$

However, when other factors are considered to determine the critical stoichiometric ratio, e.g. unequal reactivity of *o* and *p* positions or presence of important substitution effects in both phenol and formaldehyde, it may be shown that[5]:

$$(F/Ph) < 0.90 \quad \text{(actual)} \quad (3)$$

This ratio was known empirically by the industry long before the foundation of the statistics of polymerization reactions[1–4].

For the case of a diepoxide (B_2) reacting with a diamine (A_4), the prepolymerization technique may be used either to decrease the gel point, and consequently the residence time in a heated mould, or to vary the conditions under which the segregation of an elastomeric phase is produced. An experimental study of this second possibility is presented elsewhere[6]. It is therefore of interest to simulate this particular two-step polymerization.

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DIEPOXIDE (B_2) – DIAMINE (A_4) POLYMERIZATION

The stoichiometric ratio of functionalities is defined as:

$$r \text{ (eq.amine/eq.epoxy)} = 4A_4/2B_2 \quad (4)$$

For a stoichiometric mixture ($r=1$), and assuming an ideal polymerization, the conversion at the gel point is given by[1–4]:

$$p_{gel} = \{1/[(f-1)(g-1)]\}^{1/2} = 0.577 \quad (5)$$

The main non-ideality in these systems is the presence of substitution effects. Usually, the secondary amine hydrogen reacts at a slower rate than the primary amine hydrogen, the reactivity ratio k_2/k_1 depending on the chemical nature of the particular diamine[7]. For $k_2/k_1=1$ (ideal system illustrated by the behaviour of ethylene diamine[8,9]), $p_{gel}=0.577$. For $k_2/k_1=0.4$ (illustrated by the particular behaviour of 4,4′-diamino-diphenylsulphone[10] and 4,4′-diamino-3,3′-dimethyldi-cyclohexylmethane[11]), $p_{gel}=0.602$. For the limiting case of $k_2/k_1 \to 0$, $p_{gel}=0.618$. Most of the experimental values of p_{gel} reported for diepoxide–diamine systems[12] are close to 0.60, as theoretically predicted. Thus, gelation of stoichiometric systems occurs at a very narrow conversion range close to 0.60. The situation is quite different for polymerizations carried out in two steps, as will be shown.

Two cases will be considered, differing in whether epoxy or amine is in excess in the first stage. For both cases the ideal situation ($k_2/k_1=1$) will be analysed first because it leads to an analytical solution. The general situation will then be discussed through a numerical solution of the kinetic equations.

Epoxy excess

In order to avoid gelation during the first stage, the stoichiometric ratio must be less than the critical ratio. According to equation (1):

$$r < 1/3 \quad (6)$$

meaning that more than three epoxy equivalents per amine equivalent must be used in the first step.

Calculation of effective average functionality of epoxy–amine prepolymer after completion of the first stage. At the end of the first stage, the conversion of amine hydrogens is $p_A=1$, whereas the conversion of epoxy groups is limited by the stoichiometric ratio, $p_B=r$. The effective average functionality of the epoxy prepolymer, g_e, may be calculated by applying the method developed by Miller *et al.*[13].

An unreacted B-site is chosen at random. Let S_B^{in} equal the functionality seen looking in from the B-site, i.e. the additional number of unreacted B-sites on the molecule to which the randomly chosen B-site belongs. Then:

$$g_e = 1 + E(S_B^{in}) \quad (7)$$

$E(S_B^{in})$ is evaluated from the recursive algorithm developed by Macosko and Miller[14]. Thus

$$E(S_B^{in}) = E(S_B^{out}) \quad (8)$$

where S_B^{out} is the number of unreacted B-sites seen when looking out from a B-site. If B has not reacted, $S_B^{out}=1$ while if it has reacted $S_B^{out}=S_A^{in}$. Then:

$$E(S_B^{out}) = (1-p_B) + p_B E(S_A^{in}) = 1 - r + rE(S_A^{in}) \quad (9)$$

Similarly:

$$E(S_A^{in}) = 3E(S_A^{out}) \quad (10)$$

As all As are reacted:

$$E(S_A^{out}) = E(S_B^{in}) \quad (11)$$

Solving equations (8) to (11), we get:

$$E(S_B^{in}) = (1-r)/(1-3r) \quad (12)$$

Replacing into equation (7), we obtain:

$$g_e = (2-4r)/(1-3r) \quad (13)$$

It is seen that for $r=r_c=1/3$, $g_e \to \infty$ because a giant molecule (gel) is produced at the end of the first stage.

Calculation of gelation in the second stage for an ideal polymerization ($k_2/k_1=1$). The second stage is started by adding the necessary amount of amine to produce a stoichiometric mixture. However, in order to give more flexibility to the system it is convenient to consider the possibility of adding both fresh epoxy monomer and the amount of amine necessary to obtain stoichiometry. The epoxy added in the second stage may be used to reduce the initial viscosity to a convenient level. Let us call:

$$\phi_E = (B_2)_2/(B_2)_1 \quad (14)$$

the ratio of epoxy equivalents added in second and first stages ($\phi_E=0$ gives the typical two-stage system).

The diamine amount necessary to get a stoichiometric mixture is given by

$$4(A_4)_1 + 4(A_4)_2 = 2(B_2)_1 + 2(B_2)_2 \quad (15)$$

where the subscripts 1 and 2 refer to the first and second stages.

By dividing equation (15) by $2(B_2)_1$, we get:

$$(A_4)_2 = (1 + \phi_E - r)(B_2)_1/2 \quad (16)$$

The initial mixture at the start of the second stage consists of a B_g epoxy prepolymer with an effective functionality g_e and a number of unreacted sites equal to $2(B_2)_1(1-r)$, a B_2 diepoxide with a number of unreacted functionalities equal to $2(B_2)_2$, and a diamine A_4 with a number of unreacted amine hydrogens equal to $4(A_4)_2$.

Two different conversions of epoxides may be defined. One is the overall conversion of epoxy functionalities, p_B, while the other is the conversion of unreacted epoxides present at the beginning of the second stage, $(p_B)_2$. While $(p_B)_2=0$ at the start of the second stage, p_B is given by:

$$p_B(0) = 2(B_2)_1 r/[2(B_2)_1 + 2(B_2)_2] = r/(1+\phi_E) \quad (17)$$

We now apply the Macosko–Miller recursive algorithm[14] to find the conversion at gelation for the second stage. Since the system is stoichiometric, $(p_B)_2 = (p_A)_2 = p$. The average weight pendant from a B-site when looking out from the molecule to which it belongs, is given by:

$$E(W_B^{out}) = pE(W_A^{in}) \quad (18)$$

In turn:

$$E(W_A^{in}) = M_{A4} + 3E(W_A^{out}) \quad (19)$$

where M represents the molar mass of a particular species, e.g. A4. In order to calculate the weight W_A^{out} one has to evaluate the probability of joining a B-site

located either on a B_g or on a B_2. This is given by the relative amount of B-sites available on both types of molecules. Thus:

Probability of joining a B-site located on a B_g:

$$2(B_2)_1(1-r)/[2(B_2)_1(1-r)+2(B_2)_2]=(1-r)/(1-r+\phi_E)$$

Probability of joining a B-site located on a B_2:

$$2(B_2)_2/[2(B_2)_1(1-r)+2(B_2)_2]=\phi_E/(1-r+\phi_E)$$

Then:

$$E(W_A^{out})=[p/(1-r+\phi_E)][(1-r)E(W_{B_g}^{in})+\phi_E E(W_{B_2}^{in})] \quad (20)$$

$$E(W_{B_g}^{in})=M_{B_g}+(g_e-1)E(W_B^{out}) \quad (21)$$

$$E(W_{B_2}^{in})=M_{B_2}+E(W_B^{out}) \quad (22)$$

Solving the system of equations (18) to (22), replacing equation (13), and looking for the condition at which all $E(W)$s go to infinite (gelation), we get:

$$p_{gel}=\{(1-r+\phi_E)/(3[(1-r)^2/(1-3r)+\phi_E])\}^{1/2} \quad (23)$$

In order to evaluate the conversion referred to the overall concentration of epoxides, p_{Bgel}, we make:

$$p_{Bgel}=p_B(0)$$
$$+p_{gel}[2(B_2)_1(1-r)+2(B_2)_2]/[2(B_2)_1+2(B_2)_2] \quad (24)$$

Replacing equations (14), (17) and (23) into equation (24), and rearranging, we get:

$$p_{Bgel}=r/(1+\phi_E)+(1-r+\phi_E)^{3/2}/\{3^{1/2}(1+\phi_E)$$
$$\times[\phi_E+(1-r)^2/(1-3r)]^{1/2}\} \quad (25)$$

Figure 1 shows the overall conversion of epoxides at gelation, p_{Bgel} (full lines), and gel conversion of the unreacted epoxides present at the beginning of the second stage, p_{gel} (dashed lines), as a function of the epoxy monomer added in first and second stages, ϕ_E. As only the epoxy–amine reaction is allowed to take place, the final network will be the same independently of the path selected to perform the polymerization. However, the extent of reaction at gelation shows a significant variation depending on the initial stoichiometric ratio used to prepare the prepolymer. The one-stage polymerization is simulated for $r=0$, leading to $p_{Bgel}=p_{gel}=0.577$. When r gets closer to r_c, gelation is significantly advanced. The epoxy conversion in the second stage necessary to attain gelation shows a monotonous increase with ϕ_E, i.e. the more epoxy monomer is added in the second stage, the further conversion must be advanced to reach gelation. However, the overall epoxy conversion goes through a minimum. This arises simply due to the counterbalance between the decrease in the overall conversion when increasing ϕ_E and the need to increase the extent of reaction to attain the gel.

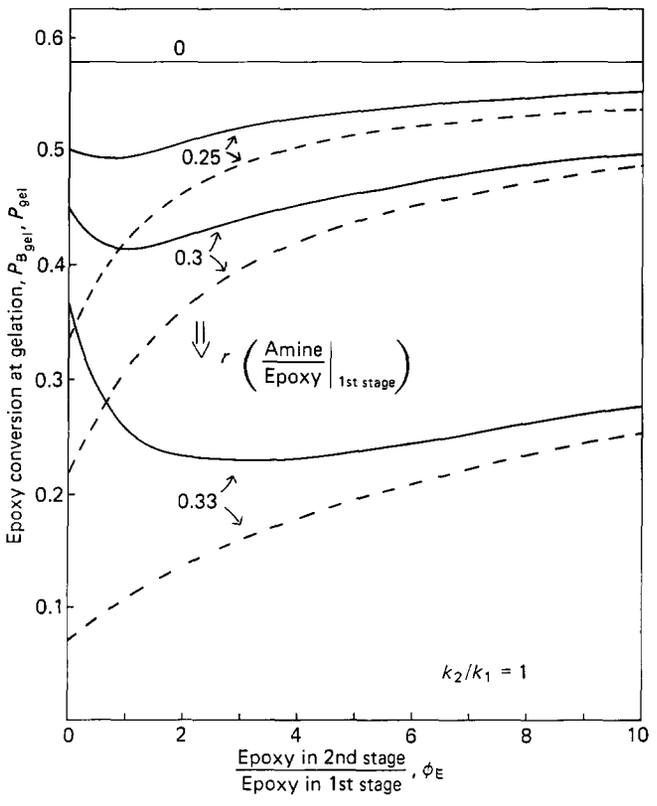

Figure 1 Overall conversion of epoxides at gelation, p_{Bgel} (——), and gel conversion of the unreacted epoxides present at the beginning of the second stage, p_{gel} (– – –), as a function of the ratio of epoxy monomer added in first and second stages, ϕ_E. Curves represent different stoichiometric ratios, r, used in the first stage. The whole diagram is valid for an ideal polymerization ($k_2/k_1=1$)

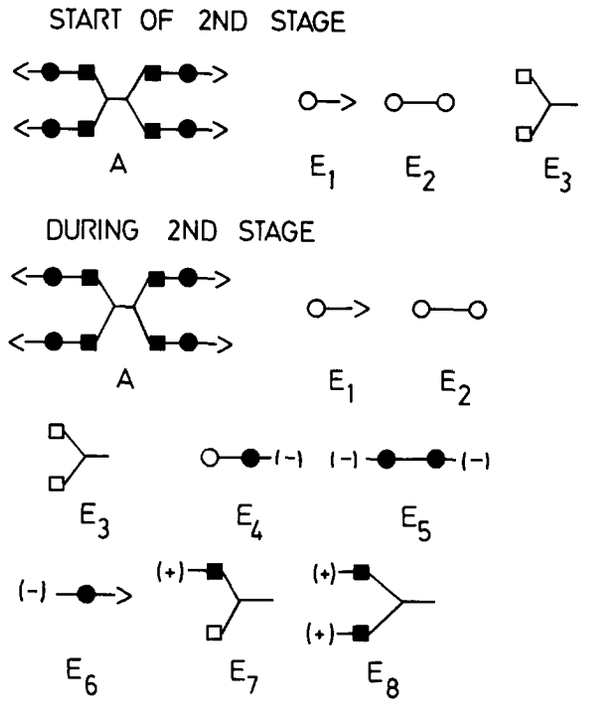

Figure 2 Different fragments present during the second stage in a system containing an initial epoxy excess. A = completely reacted diamine at the end of the first stage; E_1 = unreacted half of a diepoxide monomer attached to fragment A (arrows are joined among themselves); E_2 = diepoxide monomer added at the start of the second stage; E_3 = half of the diamine monomer added at the start of the second stage (segments are joined among themselves); E_4 = partially reacted E_2 attached to an E_7 or E_8 fragment, (–) bonds are joined to (+) bonds; E_5 = completely reacted E_2; E_6 = reacted E_1; E_7 = partially reacted E_3; E_8 = completely reacted E_3

Calculation of gelation in the second stage for a non-ideal polymerization (arbitrary value of k_2/k_1*).* Now we need a combination of kinetic and statistical methods to follow the network build-up. A convenient method is the fragment approach[15]. The most important criterion is to identify fragments arising from the first stage separately from those generated in the second stage. *Figure 2* shows a possible identification that preserves the stage at which fragments were produced.

Fragment A represents the completely reacted diamine monomer with half of reacted diepoxides attached to its

reactive sites. The number of A fragments is given by:

$$A=(B_2)_1 r/2 \quad (26)$$

as arises from equation (4). The amount of A fragments does not vary along the second stage.

Fragment E_1 represents an unreacted half of a diepoxide monomer attached to the A structure (arrows are joined among themselves). Its amount at the beginning of the second stage is given by:

$$E_1(0)=2(B_2)_1(1-r) \quad (27)$$

E_1 is progressively converted to E_6 along the second stage.

Fragment E_2 represents the fresh diepoxide monomer added at the start of the second stage. Its amount is given by

$$E_2(0)=(B_2)_1\phi_E \quad (28)$$

as results from equation (14). E_2 is converted to E_4 and E_5 as polymerization proceeds.

Fragment E_3 represents half of a diamine monomer added at the start of the second stage. The number of E_3 fragments is given by:

$$E_3(0)=2(A_4)_2=(B_2)_1(1+\phi_E-r) \quad (29)$$

as results from equation (16). E_3 is transformed into E_7 and E_8 during the second stage.

The resulting network is built up by joining (+) bonds with (−) bonds, arrows among themselves, and segments issuing from half-diamine fragments among themselves. In this way, bonds produced in both stages preserve their individuality.

The interconversion among different fragments may be calculated by the following kinetic equations:

$$-dE_1/dt=E_1(2k_1E_3+k_2E_7) \quad (30)$$

$$-dE_2/dt=2E_2(2k_1E_3+k_2E_7) \quad (31)$$

$$-dE_3/dt=2k_1E_3(E_1+2E_2+E_4) \quad (32)$$

$$dE_4/dt=(2E_2-E_4)(2k_1E_3+k_2E_7) \quad (33)$$

$$dE_5/dt=E_4(2k_1E_3+k_2E_7) \quad (34)$$

$$dE_6/dt=E_1(2k_1E_3+k_2E_7) \quad (35)$$

$$dE_7/dt=(2k_1E_3-k_2E_7)(E_1+2E_2+E_4) \quad (36)$$

$$dE_8/dt=k_2E_7(E_1+2E_2+E_4) \quad (37)$$

By dividing all kinetic equations by one of them, e.g. equation (30), the concentration of every fragment may be numerically calculated as a function of conversion and the single parameter (k_2/k_1).

The epoxy conversion in the second stage is calculated as:

$$p=(E_4+2E_5+E_6)/[E_1(0)+2E_2(0)] \quad (38)$$

whereas the overall conversion of epoxides in both stages is given by:

$$p_B=(4A+E_4+2E_5+E_6)/[4A+E_1(0)+2E_2(0)] \quad (39)$$

Once the concentration of every fragment is known as a function of conversion, calculation of different network parameters is performed by rebuilding the whole structure through appropriate linkages[15]. Details of the calculations are given in a previous paper[15]. The network gels, when average weights joined to arrows, (+) bonds, (−) bonds and half-diamine segments, go to infinity. This

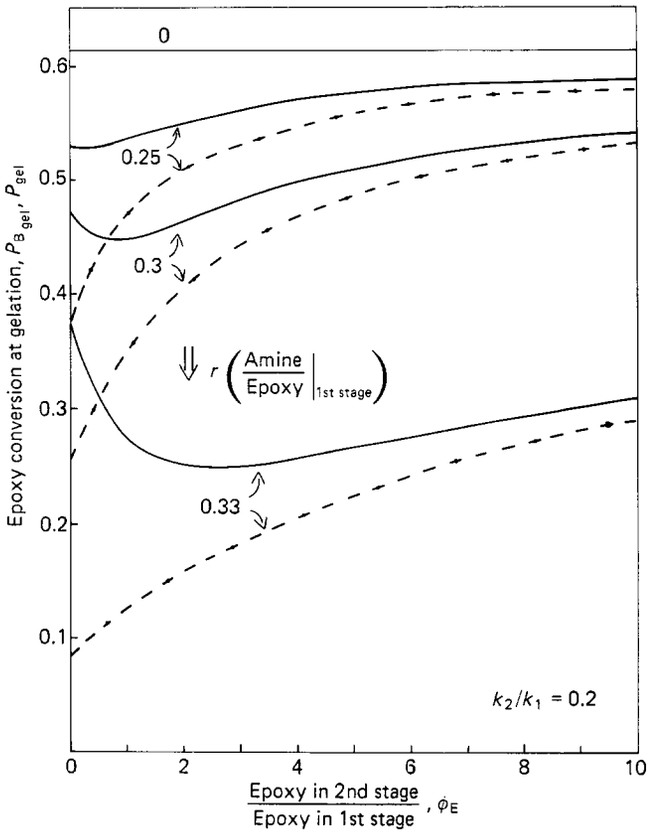

Figure 3 Overall conversion of epoxides at gelation, p_{Bgel} (——), and gel conversion of the unreacted epoxides present at the beginning of the second stage, p_{gel} (– – –), as a function of the ratio of epoxy monomer added in first and second stages, ϕ_E. Curves represent different stoichiometric ratios, r, used in the first stage. The diagram is valid for a non-ideal polymerization with $k_2/k_1=0.2$

condition is fulfilled when:

$$2\left\{\frac{(E_6^*)^2}{(1-3r)}+2E_5^*\right\}\left\{\frac{1}{(1+\phi_E-r)}+\frac{E_8^*}{[p_{Bgel}(1+\phi_E)-r]^2}\right\}=1 \quad (40)$$

where $E_i^*=E_i/[2(B_2)_1]$.

It was numerically proved that equation (40) gave exactly the same results as equation (25), when $k_2/k_1=1$. *Figure 3* shows calculations performed for $k_2/k_1=0.2$, plotted in a similar way to *Figure 1*. Results are qualitatively similar to those for the ideal case. For example, by making a prepolymer at $r=0.3$, and using the same amount of epoxy monomer in both stages ($\phi_E=1$), conversion at gelation may be reduced from 0.613 to 0.352 (or 0.447 if the overall value is considered).

Amine excess

In this case, the critical stoichiometric ratio to avoid gelation depends on the (k_2/k_1) value[16]. It varies from $r_c=3$ when $k_2/k_1=1$ to $r_c=2$ when $k_2/k_1\to 0$. The experimental determination of r_c constitutes a convenient way to determine the value of the k_2/k_1 ratio[9,10].

Calculations for an ideal polymerization ($k_2/k_1=1$). For this situation we can again find an analytical solution. As $r_c=3$, the first stage of the polymerization must be carried out with an amine excess such that $r>3$. At the end of this stage, the conversion of epoxides is $p_B=1$ and,

due to stoichiometry, the extent of reaction of amine hydrogens is $p_A = 1/r$.

The effective average functionality of the amine prepolymer may be calculated as for the case with epoxy excess. Thus:

$$f_e = 1 + E(S_A^{in}) \quad (41)$$

$$E(S_A^{in}) = 3E(S_A^{out}) \quad (42)$$

$$E(S_A^{out}) = (1-p_A) + p_A E(S_B^{in}) = 1 - (1/r)[1 - E(S_B^{in})] \quad (43)$$

$$E(S_B^{in}) = E(S_B^{out}) \quad (44)$$

$$E(S_B^{out}) = E(S_A^{in}) \quad (45)$$

Solving the system of equations (42) to (45) and replacing the value of $E(S_A^{in})$ into equation (41), we get:

$$f_e = (4r-6)/(r-3) \quad (46)$$

For $r = r_c = 3, f_e \to \infty$ because gelation is attained at the end of the first stage.

The possibility of adding extra amine in the second stage, together with the necessary epoxy to obtain stoichiometry, is taken into account. The extra amine is expressed by:

$$\phi_A = (A_4)_2/(A_4)_1 \quad (47)$$

which gives the ratio of amine equivalents added in the second and first stages ($\phi_A = 0$ gives the typical two-stage system).

The amount of epoxy necessary to obtain stoichiometry is calculated from:

$$4(A_4)_1 + 4(A_4)_2 = 2(B_2)_1 + 2(B_2)_2 \quad (48)$$

Dividing equation (48) by $4(A_4)_1$, we get:

$$(B_2)_2 = (1 + \phi_A - r^{-1})2(A_4)_1 \quad (49)$$

The initial mixture consists of an A_f amine prepolymer with effective functionality f_e and a number of unreacted sites equal to $4(A_4)_1(1-r^{-1})$, an A_4 diamine with a number of unreacted functionalities equal to $4(A_4)_2$, and a B_2 diepoxide with a number of unreacted sites equal to $2(B_2)_2$.

Two different conversions of amine hydrogens may be defined. One is the overall conversion of amine hydrogens, p_A, while the other is the conversion of unreacted amine hydrogens present at the beginning of the second stage, $(p_A)_2$. While $(p_A)_2 = 0$ at the start of the second stage, p_A is given by:

$$p_A(0) = 4(A_4)_1(1/r)/[4(A_4)_1 + 4(A_4)_2]$$
$$= 1/[r(1+\phi_A)] \quad (50)$$

The Macosko–Miller recursive method[14] may be conveniently applied to find the gelation condition. Since the system is stoichiometric, $(p_A)_2 = (p_B)_2 = p$. Then:

$$E(W_A^{out}) = pE(W_B^{in}) \quad (51)$$

$$E(W_B^{in}) = M_{B_2} + E(W_B^{out}) \quad (52)$$

In order to evaluate the weight W_B^{out} one has to calculate the probability of joining an A-site located either on an A_f or on an A_4. This is given by the relative amount of A-sites available on both types of molecules. Then:

Probability of joining an A-site located on an A_f:

$$4(A_4)_1(1-r^{-1})/[4(A_4)_1(1-r^{-1}) + 4(A_4)_2]$$
$$= (r-1)/[r(1+\phi_A) - 1]$$

Probability of joining an A-site located on an A_4:

$$4(A_4)_2/[4(A_4)_1(1-r^{-1}) + 4(A_4)_2] = r\phi_A/[r(1+\phi_A) - 1]$$

Then, we get:

$$E(W_B^{out}) = \{p/[r(1+\phi_A) - 1]\}$$
$$\times \{(r-1)E(W_{A_f}^{in}) + r\phi_A E(W_{A_4}^{in})\} \quad (53)$$

$$E(W_{A_f}^{in}) = M_{A_f} + (f_e - 1)E(W_A^{out}) \quad (54)$$

$$E(W_{A_4}^{in}) = M_{A_4} + 3E(W_A^{out}) \quad (55)$$

Solving the system of equations (51) to (55), replacing equation (46), and looking for the condition at which all $E(W)$s go to infinite (gelation), we get:

$$p_{gel} = \{[r(1+\phi_A) - 1]/(3[r\phi_A + (r-1)^2/(r-3)])\}^{1/2} \quad (56)$$

In order to calculate the conversion referred to the overall concentration of amine hydrogens, p_{Agel}, we state:

$$p_{Agel} = p_A(0) + p_{gel}[4(A_4)_1(1-r^{-1}) + 4(A_4)_2]/$$
$$[4(A_4)_1 + 4(A_4)_2] \quad (57)$$

Replacing equations (47), (50) and (56) into equation (57), and rearranging, we get:

$$p_{Agel} = \frac{1}{r(1+\phi_A)}\left\{1 + \left[\frac{[r(1+\phi_A)-1]^3}{3[r\phi_A + (r-1)^2/(r-3)]}\right]^{1/2}\right\} \quad (58)$$

Figure 4 shows the overall conversion of amine hydrogens at gelation, p_{Agel} (full lines), and gel conversion of the unreacted amine hydrogens present at the beginning of the second state, p_{gel} (dashed lines), as a function of the diamine ratio added in the first and second

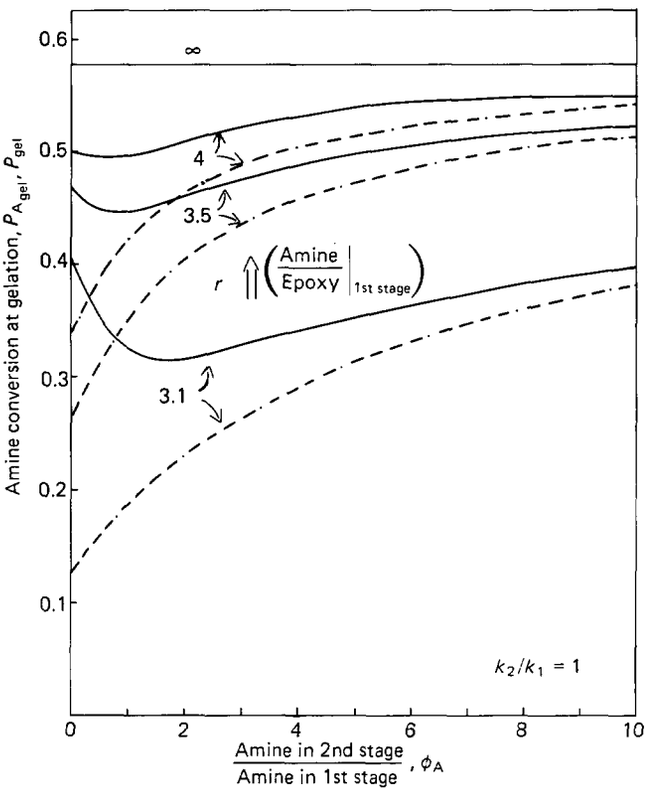

Figure 4 Overall conversion of amine hydrogens at gelation, p_{Agel} (——), and gel conversion of the unreacted amine hydrogens present at the beginning of the second stage, p_{gel} (– – –), as a function of the diamine ratio added in first and second stages, ϕ_A. Curves represent different stoichiometric ratios, r, used in the first stage. The diagram is valid for an ideal polymerization ($k_2/k_1 = 1$).

stages, ϕ_A. For $r \to \infty$, the one stage polymerization is simulated and $p_{Agel} = p_{gel} = 0.577$. An amine prepolymer prepared with $r = 3.5$, leads to gelation in the second stage for $p_{gel} = 0.258$ (for $\phi_A = 0$). This means that the use of an amine prepolymer ($r = 3.5$) decreases the extent of reaction at gelation from 0.577 (one-stage polymerization) to 0.258 (two-stage polymerization), leading to exactly the same final material.

For diamines of very low viscosity, prepolymerization may constitute a practical way to shorten residence times in heated moulds (as in reaction injection moulding (RIM) or pultrusion techniques). If necessary, extra diamine may be added in the second stage to decrease viscosity and still achieve relatively low conversions at gelation, e.g. for $\phi_A = 1$ and $r = 3.5$, $p_{gel} = 0.354$. The minimum in p_{Agel} curves is explained similarly to the case of an initial epoxy excess.

Calculations for a non-ideal polymerization ($k_2/k_1 \neq 1$). Again we use a fragment approach to analyse the non-ideal case. However, it is now necessary to simulate both stages separately as the difference in reactivities influences the distribution of fragments arising from the first stage. *Figure 5* shows the fragments present during the first stage in a system containing an initial amine excess. The initial concentration of E_2 and E_3 fragments is given by:

$$E_2(0) = (B_2)_1 \tag{59}$$

$$E_3(0) = 2(A_4)_1 = (B_2)_1 r \tag{60}$$

The concentration of different fragments along the first stage may be calculated using the following kinetic equations:

$$-dE_2/dt = 2E_2(2k_1E_3 + k_2E_7) \tag{61}$$

$$-dE_3/dt = 2k_1E_3(2E_2 + E_4) \tag{62}$$

$$dE_4/dt = (2E_2 - E_4)(2k_1E_3 + k_2E_7) \tag{63}$$

$$dE_5/dt = E_4(2k_1E_3 + k_2E_7) \tag{64}$$

$$dE_7/dt = (2k_1E_3 - k_2E_7)(2E_2 + E_4) \tag{65}$$

$$dE_8/dt = k_2E_7(2E_2 + E_4) \tag{66}$$

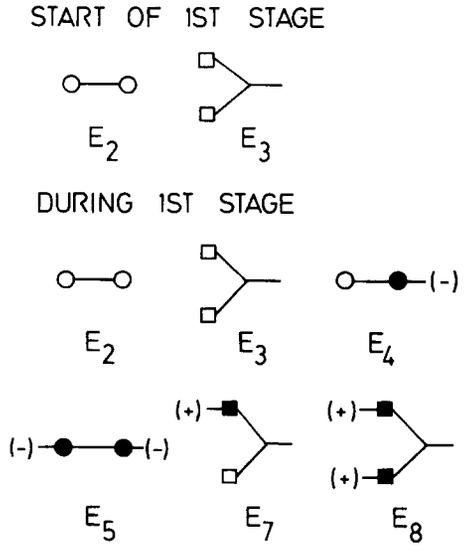

Figure 5 Different fragments present during the first stage in a system containing an initial amine excess. Symbols are the same as in *Figure 2*

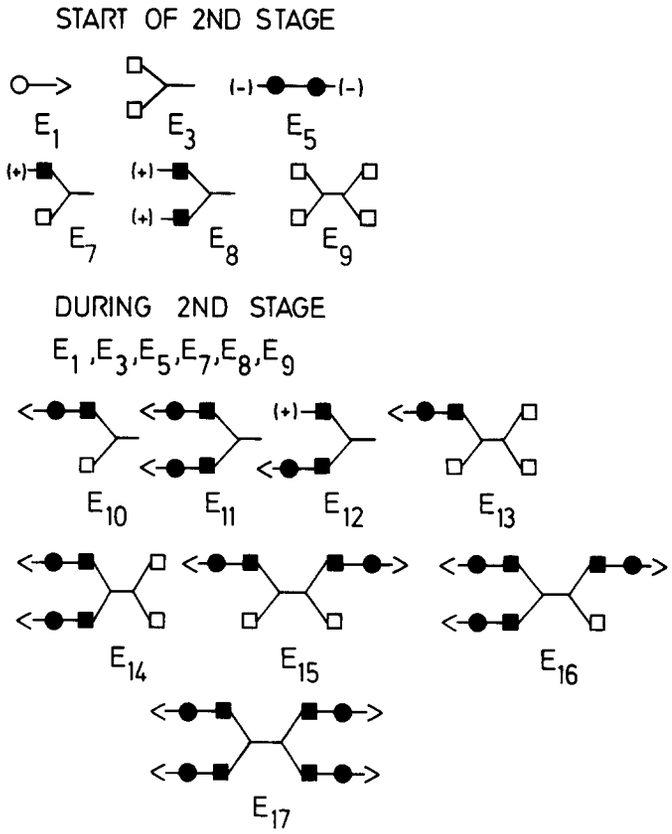

Figure 6 Different fragments present during the second stage in a system containing an initial amine excess. Symbols are similar to those in *Figure 2*. E_9 = unreacted diamine monomer; E_{13} to E_{17} = partially or totally reacted fragments arising from E_9, (+) bonds are joined to (−) bonds, arrows among themselves as well as segments issuing from half-diamine fragments (as E_3)

Solving the system of equations (61) to (66), the concentration of fragments E_3, E_5, E_7 and E_8 may be obtained for a complete conversion of epoxides ($E_2 = E_4 = 0$), and arbitrary values of r and (k_2/k_1).

Fragments to be considered during the second stage are shown in *Figure 6*. It has been necessary to introduce the whole structure of the diamine monomer, in several reaction states, to preserve the individuality of bonds generated in the first and second stages of the polymerization: (+) bonds are joined to (−) bonds and arrows as well as half-diamine segments among themselves.

The amount of fragments E_3, E_5, E_7 and E_8 at the start of the second stage is the same as obtained at the end of the first stage. The amount of diamine monomer at the beginning of the second stage is obtained from equations (4) and (47):

$$E_9(0) = (B_2)_1 r \phi_A / 2 \tag{67}$$

whereas the initial number of E_1 fragments arises from equations (4) and (49):

$$E_1(0) = 2(B_2)_2 = 2(B_2)_1[r(1 + \phi_A) - 1] \tag{68}$$

The evolution of the system in the second stage may be calculated by the following kinetic equations:

$$-dE_1/dt = E_1[2k_1(E_3 + 2E_9 + E_{13} + E_{14}) + k_2(E_7 + E_{10} + E_{13} + 2E_{15} + E_{16})] \tag{69}$$

$$-dE_3/dt = 2k_1E_1E_3 \tag{70}$$

$$-dE_7/dt = k_2E_1E_7 \tag{71}$$

$$-dE_9/dt = 4k_1E_1E_9 \quad (72)$$

$$dE_{10}/dt = E_1(2k_1E_3 - k_2E_{10}) \quad (73)$$

$$dE_{11}/dt = k_2E_1E_{10} \quad (74)$$

$$dE_{12}/dt = k_2E_1E_7 \quad (75)$$

$$dE_{13}/dt = 2k_1E_1(2E_9 - E_{13}) - k_2E_1E_{13} \quad (76)$$

$$dE_{14}/dt = k_2E_1E_{13} - 2k_1E_1E_{14} \quad (77)$$

$$dE_{15}/dt = 2E_1(k_1E_{13} - k_2E_{15}) \quad (78)$$

$$dE_{16}/dt = 2k_1E_1E_{14} + k_2E_1(2E_{15} - E_{16}) \quad (79)$$

$$dE_{17}/dt = k_2E_1E_{16} \quad (80)$$

Dividing equations (70) to (80) by equation (69), the concentration of every fragment may be numerically calculated as a function of conversion and (k_2/k_1).

The amine conversion in the second stage is given by:

$$p = [1/E_1(0)](E_{10} + 2E_{11} + E_{12} + E_{13} + 2E_{14} + 2E_{15} + 3E_{16} + 4E_{17}) \quad (81)$$

while the overall conversion of amine hydrogens along both stages is expressed by:

$$p_A = [E_7(0) + 2E_8 + pE_1(0)]/[E_7(0) + 2E_8 + E_1(0)] \quad (82)$$

But as $E_7(0) + 2E_8 = 2(B_2)_1$, using equations (68) and (82), we get:

$$p_A = \{1 + p[r(1 + \phi_A) - 1]\}/\{r(1 + \phi_A)\} \quad (83)$$

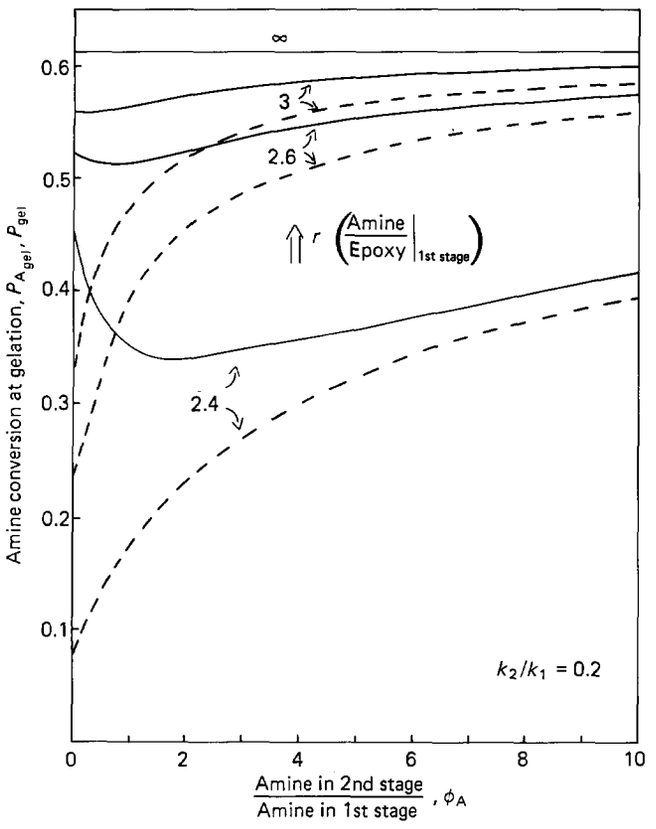

Figure 7 Overall conversion of amine hydrogens at gelation, p_{Agel} (——), and gel conversion of the unreacted amine hydrogens present at the beginning of the second stage, p_{gel} (– – –), as a function of the diamine ratio added in first and second stages, ϕ_A. Curves represent different stoichiometric ratios, r, used in the first stage. The diagram is valid for a non-ideal polymerization with $k_2/k_1 = 0.2$

Once the concentration of every fragment is known as a function of conversion, the gel condition may be calculated using the recursive method previously described[15]. Details of the calculations are given in a previous paper[15]. Let us simply say that the gel condition arises when average weights joined to arrows, (+) bonds, (−) bonds and half-diamine segments go to infinity.

Numerical calculations for $k_2/k_1 = 1$ gave the same results as the analytical solution. *Figure 7* shows results obtained for $k_2/k_1 = 0.2$, plotted in a similar way to *Figure 4*. Although results are qualitatively similar, it may be seen that allowed r values are considerably lower than for the ideal case. For example, a prepolymer prepared with an amine excess equal to $r = 2.6$, gels in the second stage at $p_{gel} = 0.23$ (for $\phi_A = 0$). The same material prepared in one stage ($r \to \infty$), shows an extent of reaction at gelation equal to $p_{gel} = 0.613$. This significant variation in the gel conversion may be used with advantage to modify the design of the particular cure process used to produce the final material.

CONCLUSIONS

Although prepolymerization techniques are used for several applications in the field of thermosetting polymers, they are normally not considered as a general alternative when designing cure processes. Here we have analysed the possible application for diepoxide–diamine systems. Of practical significance is the fact that the processing of diepoxide–diamine systems by conventional techniques (RIM, pultrusion, autoclave cure, etc.) may be considerably varied if the prepolymerization procedure is adopted. For example, by making a prepolymer at $r = 0.3$, and using the same amount of epoxy monomer in both stages ($\phi_E = 1$), the extent of reaction at gelation may be reduced from 0.577 to 0.310 (or 0.413 if the overall value is considered), while always obtaining the same final material. In this case, prepolymerization may be used to decrease demoulding times. Another possibility arising from a change in the polymerization path is to obtain different morphologies of a rubbery phase segregated during polymerization[6].

It has been shown that the Macosko–Miller recursive method[14] may be easily used to predict the extent of reaction at gelation for two-stage ideal systems $(k_2/k_1 = 1)$. For the general case, the fragment approach[15] constitutes a convenient way to preserve the identity of bonds generated in both stages, leading to a numerical solution through the use of a recursive algorithm.

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