

Gelation in the Curing of Epoxy Resins with Anhydrides

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Summary

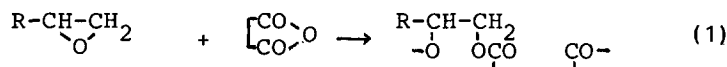
The statistical theory of branching processes has been used in an analysis of gelation in the system diepoxide-cyclic anhydride-tert.-amine in step and initiated reaction mechanisms. Experimental data indicate that critical conversion depends on the concentration of tert.-amine, which suggests that a mechanism with initiation is operative.

Introduction

Although the importance of acid curing of epoxy resins equals that with polyamines, the formation and structure of cured products are much less understood. The main reasons are as follows: (1) The mechanism of reaction of the epoxy group with the anhydride group is complicated and has not been sufficiently explained. The same is true about the role played by compounds with active hydrogen (cf., e.g. MAY and TANAKA 1973, ANTOON and KOENIG 1981). (2) Only few experimental data on gelation and network formation are available, and a statistical treatment is missing.

For curing with polyamines, it has been established that each primary amino group is bifunctional and each epoxy group is monofunctional, and the reaction (if epoxy groups are not in excess) has an alternating and stepwise character; the catalyst, e.g. tert.-amine, is not bound chemically, but only accelerates the reaction (cf., e.g. LUŇÁK and DUŠEK 1975, DUŠEK et al. 1977, DUŠEK and ILAVSKÝ 1980).

The propagation brutto-reaction occurring in the curing of epoxides with cyclic anhydrides can be written as



Here, the epoxy group is bifunctional and so is the cyclic anhydride. This has led to a supposition (TANAKA and KAKIUCHI 1965) that in the base catalyzed curing

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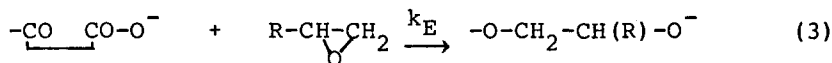
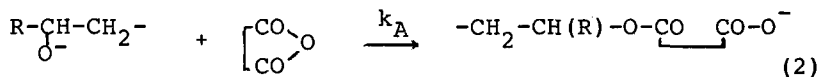
(alternating mechanism) of an equimolar mixture of tetrafunctional diepoxide with a bifunctional anhydride the critical conversion of epoxy groups α_E should approach $3^{-1/2} \approx 0.58$, a value which holds for the conversion of functionalities in a random reaction.

In this paper, we demonstrate that the situation is much more complicated, because (a) the conversion of monomers differs from that of functionalities, (b) addition of anhydride and epoxide in the propagation reaction does not proceed at the same rate, and (c) tert.-amine has not only an accelerating, but also an initiating effect and affects the chain length. We also give the results of critical conversion measurements in the system diglycidyl ether of Bisphenol A-hexahydrophthalanhydride-benzyltrimethylamine.

Mechanism of Curing Reaction

Most authors agree that the mechanism of the reaction catalyzed with tert.-amine is an anionic one. According to FISCHER (1960), the reaction is initiated by the anion formed in a reaction between anhydride and tert.-amine $R_3N^+CO-CO-O^-$; after TANAKA and KAKIUCHI (1966), the propagation is initiated by a reaction between tert.-amine and epoxide, while FEDTKE (1981) reports that tert.-amine is chemically bound to epoxide.

Irrespective of the detailed mechanism, it can be stated that (1) reaction is initiated by tert.-amine and/or anion due to an interaction of the proton donor possibly present with tert.-amine, (2) propagation proceeds via two reactions



generally, acylation is faster than the reaction between epoxide and carboxyl group, so that $k_A > k_E$, (3) there is no unambiguous view regarding the termination and regeneration of tert.-amine in which one molecule of amine may initiate growth of more than one chain (TANAKA and HUANG 1968).

The ratio of rates of binding (initiation) and regeneration of tert.-amine determines the propagation mechanism: for a relatively fast initiation, propagation approaches the anionic living polymerization, while for a fast regeneration, tert.-amine only accelerates the reactions and the mechanism corresponds to step polyaddition. These differences have a decisive influence on gelation.

Critical Conversion at Gelation

Critical conversion in the reaction between a

tetrafunctional diepoxide and a bifunctional cyclic anhydride depends not only on the molar ratio of components, but also on the reaction mechanism and on the ratio of rate constants of reactions (2) and (3). We shall demonstrate the effect of these factors for some limiting cases, using the theory of branching processes employed earlier in the description of curing of diepoxides with diamines (DUŠEK et al. 1975, DUŠEK and ILAVSKÝ 1980).

(1) Step mechanism characteristic for the fast migration of tert.-amine: The probability generating function (pgf) for the number of bonds issuing from a diepoxide or an anhydride unit in the root $F_O(\theta) = (F_{OE}(\theta_A), F_{OA}(\theta_E))$ and in the first and higher generations $F_1(\theta) = (F_{1E}(\theta_A), F_{1A}(\theta_E))$ can be written as

$$F_{OE}(\theta_A) = (e_0 + e_1\theta_A + e_2\theta_A^2)^2 \quad (4)$$

$$F_{OA}(\theta_E) = a_0 + a_1\theta_E + a_2\theta_E^2 \quad (5)$$

$$F_{1E}(\theta_A) = (e_1 + 2e_2\theta_A)(e_0 + e_1\theta_A + e_2\theta_A^2)/(e_1 + 2e_2) \quad (6)$$

$$F_{1A}(\theta_E) = (a_1 + 2a_2\theta_E)/(a_1 + 2a_2) \quad (7)$$

where e_i, a_i are fractions of epoxide and anhydride units issuing i bonds and θ is a dummy variable. The gelation condition can be derived from derivatives of pgf $F_1(\theta=1)$ in the form

$$F_{1E}'F_{1A}' = \frac{[2e_2 + (e_1 + 2e_2)^2]2a_2}{(e_1 + 2e_2)(a_1 + 2a_2)} = 1 \quad (8)$$

The fractions a_i, e_i can be expressed either through the conversion of functionalities ξ_A and ξ_E (O^-, COO^- groups being regarded as unreacted)

$$\xi_A = (a_1 + 2a_2)/2, \quad \xi_E = (e_1 + 2e_2)/2 \quad (9)$$

or through conversion of the monomer

$$\alpha_A = a_1 + a_2 = 1 - a_0, \quad \alpha_E = e_1 + e_2 = 1 - e_0 \quad (10)$$

Usually, conversions α_E and α_A are determined.

Random case: all reaction steps have the same rate ($k_A = k_E$); then the fractions a_i, e_i are coefficients of binomial expansion $((1 - \xi) + \xi)^2$: $a_0 = (1 - \xi_A)^2 = 1 - \alpha_A$,

$$a_1 = 2\xi_A(1 - \xi_A), \quad a_2 = \xi_A^2$$

Hence,

$$a_1 = [2\alpha_A(1 - \alpha_A)^{1/2}]/[1 + (1 - \alpha_A)^{1/2}] \quad \text{and}$$

$$a_2 = \alpha_A[1 - (1 - \alpha_A)^{1/2}]/[1 + (1 - \alpha_A)^{1/2}]$$

analogous relations are obtained for e_0 , e_1 and e_2 as functions of conversions ξ_E and α_E . According to Eq.(8), the gel point is described by the condition

$$3\xi_A\xi_E = \frac{3\alpha_E [1 - (1 - \alpha_A)^{1/2}]}{1 + (1 - \alpha_E)^{1/2}} = 1 \quad (11)$$

which, for the equimolar case ($\xi_A = \xi_E$, $\alpha_A = \alpha_E$) yields critical conversions

$$\xi_E = 3^{-1/2} \approx 0.58, \quad \alpha_E = (2 \times 3^{1/2} - 1)/3 \approx 0.82$$

It follows that the determined α_E (not ξ_E !) values 0.55-0.60 (TAMAKA and KAKIUCHI 1963 and 1965) should by no means indicate that all reaction steps are equally probable.

The condition (8) can be used also for non-random reactions. If reaction (2) is much faster than reaction (3) ($e_1=0$), the critical value of α_E can be shown to approach 1/2. If both reactions were much faster than the reaction between monomers ($e_1=a_1=0$), $\alpha_E \rightarrow 0$, and if reaction (3) is much slower than reaction (2) and reaction between monomers, $\alpha_E = (1 + 17^{1/2})/8 \approx 0.64$.

Whatever changes in the critical conversion may be caused by differences in relative rates of reaction steps, it is important to note that α_E should not depend on the concentration of tert.-amine.

(2) Initiated reaction. Let us assume that tert.-amine is not regenerated in the termination step. Then, each chain formed in a reaction between the epoxy group and cyclic anhydride is terminated, at one end, by a molecule of tert.-amine, and at the other, by an unreacted group. This peculiarity must be taken into account in the statistical treatment by using directed graphs with oriented vertices (cf. BUCHARD et al. 1974, DUŠEK et al. 1978). Let the left direction (subscript ℓ) always lead to the initiator molecule (I) (tert.-amine) and the right direction (subscript r) always lead to the unreacted group. The components of the pgf for units in the root (they involve also the initiator molecule I) can now be written as

$$F_{OI}(\underline{\theta}) = 1 - \alpha_I + \alpha_I \theta_{rE} \quad (12)$$

$$F_{OA}(\underline{\theta}) = 1 - \alpha_A + \alpha_A \theta_{\ell E} (\alpha_1 + \alpha_2 \theta_{rE}) \quad (13)$$

$$F_{OE}(\underline{\theta}) = f_{OE}^2 = [1 - \alpha_E + \alpha_E (p_I \theta_{\ell I} + p_A \theta_{\ell A}) (\epsilon_1 + \epsilon_2 \theta_{rA})]^2 \quad (14)$$

where α_I is conversion of the initiator, $\alpha_I = (I_0 - I)/I_0$, $\alpha_1 = a_1/(a_1 + a_2)$, $\alpha_2 = 1 - \alpha_1$; $\epsilon_1 = e_1/(e_1 + e_2)$, $\epsilon_2 = 1 - \epsilon_1$, $p_I = I_0 \alpha_I / (A_0 a_2 + I_0 \alpha_I)$, $p_A = 1 - p_I$ and I_0, A_0 are the initial number of moles of the initiator (tert.-amine) and anhydride. For growth of the tree-

-like structure, the pgf F_1 for units in the first and higher generations, are decisive and we must already discern the direction ℓ or r ; subscript 1 at F_1 is left out in what follows

$$F_I(\underline{\theta}) = 1 \quad (15)$$

$$F_{rA}(\underline{\theta}) = \alpha_1 + \alpha_2 \theta_{rE}, \quad F_{\ell A}(\underline{\theta}) = \theta_{\ell E} \quad (16)$$

$$F_{rE}(\underline{\theta}) = (\epsilon_1 + \epsilon_2 \theta_{rA}) f_{OE}, \quad F_{\ell E}(\underline{\theta}) = (p_I + p_A \theta_{\ell A}) f_{OE} \quad (17)$$

The gel point is given by Eq.(18)

$$D = \det(\delta_{kn}^{ij} - F_{kn}^{ij}) = 0 \quad (18)$$

where D is the determinant of 5th degree, δ_{kn}^{ij} is Kronecker delta (equals unity for $k=i, n=j$, and zero otherwise), and F_{kn}^{ij} are values of the derivatives of pgf $(\partial F_{kn}(\underline{\theta}) / \partial \theta_{ij})_{\underline{\theta}=1}$.

These operations yield an explicit condition for the gel point in the form

$$1 - \alpha_2 \epsilon_2 (1 + \alpha_E) + \alpha_2 p_A \epsilon_2 (1 + \alpha_E)^2 - \alpha_2^2 \alpha_E p_A \epsilon_2 - p_A (1 + \alpha_E) = 0 \quad (19)$$

Let it be assumed, further, that reaction (2) is much faster than reaction (3) (i.e. $\epsilon_1 = 0, \epsilon_2 = 1$), and that the initiation step consists in the reaction between the epoxide and the amine. To express p_A and α_2 , the composition of the chain is taken into consideration, i.e. $A_O a_1 = I_O \alpha_1$, and thus $A_O a_2 = E_O \alpha_E - I_O \alpha_I$; if moreover, the equimolar composition is considered, i.e. $A_O = E_O$, then

$$p_A = \alpha_2 = (1 - X) \quad (20)$$

where

$$X = q \alpha_I / \alpha_E, \quad q = I_O / E_O$$

The dependence of α_I on α_E is derived from the following reasoning: the initiator is consumed by the reaction with the epoxide, and the epoxide is consumed by the reaction with the initiator and with the COO^- end group. Hence, the kinetic equations can be written as

$$-dI/dt = k_I I E \quad (21)$$

$$-dE/dt = k_I I E + k_E (I_O - I) E \quad (22)$$

Their solution gives the relation ($\kappa = k_E/k_I$)

$$\alpha_E = (1 - \kappa)q\alpha_I - \kappa q \ln(1 - \alpha_I) \quad (23)$$

and Eq.(19), using Eqs (20) and (23), gives the gel condition in the form

$$2(1 - X)(1 + \alpha_E) - (1 - X)^2(1 + 2\alpha_E) = 1 \quad (24)$$

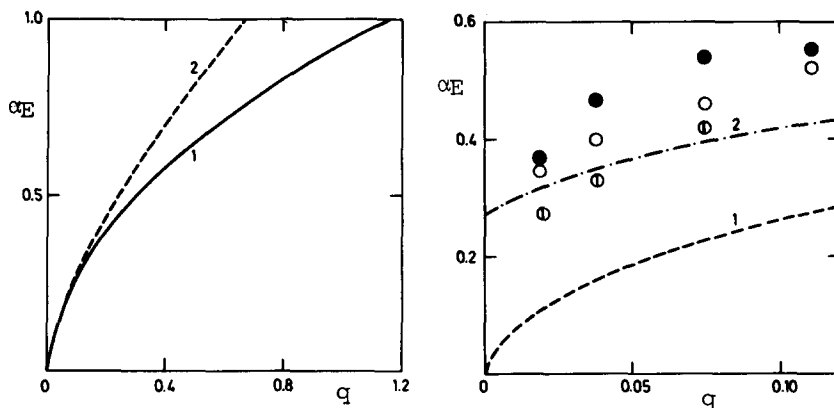


Fig.1 Dependence of the critical conversion of epoxy groups α_E on the initial molar ratio of initiator to epoxide q for an equimolar ratio epoxide/anhydride 1 the same rate of initiation and propagation, $\kappa = 1$; 2 much faster initiation, $\kappa = 0$.

Fig.2 Dependence of the critical conversion of epoxide groups α_E in an equimolar system DGEBA-HHPA catalyzed with BDMA on the initial molar ratio amine/epoxide, \circ 110°C, 50% xylene, titration, \bullet 80°C, bulk, IR analysis, \emptyset 110°C, bulk, IR analysis; curve 1 theory (Eq.(24)), curve 2 theory (Eq.(24)) taking into account 2% of acid present in HHPA.

Fig.1 shows the dependence of the critical conversion of epoxy groups on $q = I_0/E_0$ for the same rate of initiation and propagation ($\kappa = 1$, $\alpha_I = 1 - \exp(-\alpha_E/q)$) and for a much faster initiation ($\kappa = 0$, $\alpha_I = \alpha_E/q$); if propagation is much faster than initiation ($\kappa \rightarrow \infty$), α_E converges to zero at any q .

Thus, for all real cases the dependence of critical conversion on the concentration of tert.-amine is quite evident.

Gelation in the system diglycidyl ether of Bisphenol A (DGEBA)-hexahydrophthalanhydride (HHPA)-benzyl dimethylamine (BDMA)

The gel time was determined from solubility measurements of the reacting system (cf. LUŇAK and DUŠEK

1975), the dependence of α_E on time was determined either by the titration method (pyridine-hydrochloride method with a simultaneous determination of the acid number) or by IR spectrometry from the ratio of absorbances $A_{2.205}/A_{1.668}$ (KLABAN et al.1968). The dependence of critical conversion on the concentration of BDMA (Fig.2) is obvious, but the experimental points lie, nevertheless, above the theoretical curve for $\kappa = 1$ and $\kappa = 0$ (the effect of κ ($\kappa \leq 1$) on α_E is small in this range). The difference may well be due to the assumed approximations in the reaction mechanism, but the possible effect of purity of the compounds used must also be considered. The purity of DGEBA was 97% and the relevant average functionality was ~ 3.9 instead of 4; the purity of recrystallized HHPA was 98% (1.9% acid). It can be shown that the reduced functionality has no important effect on the critical value of α_E , but that $\sim 2\%$ of acid in HHPA may considerably affect gelation, because a compound containing active hydrogen acts as initiator. If the effect of acid and BDMA were additive, curve 2 would be obtained (Fig.2), which lies roughly in the range of experimental data.

Thus, the gel data indicate an initiation mechanism of the reaction and the concentration of compounds containing active hydrogen is important. The analysis of gelation also shows the necessity of a deeper insight into the reaction mechanism as a condition for understanding the network formation in curing. Measurements of critical conversions may contribute to the elucidation of this mechanism.

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