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Kinetics and mechanism of the epoxide–amine polyaddition[1]

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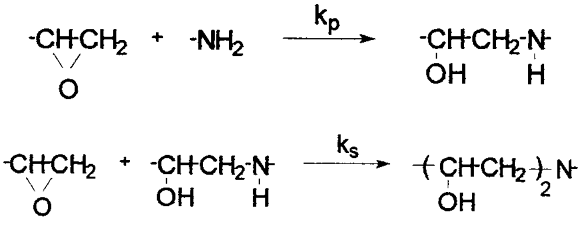
Abstract

The mechanism and kinetics of the epoxide–amine polyaddition reaction have been studied by isothermal and scanning DSC measurements. The initial concentrations of the reactants (epoxides: bisphenol-A-diglycidyl ether (DGEBA) and phenyl glycidyl ether (PGE), amines: N,N'-dibenzylethylenediamine (DBED) and aniline) in our model systems have been strongly varied. The suggested kinetic model describes the reaction behavior of mixtures with any initial epoxide/amine ratios over the whole range of cure by a single parameter set. To find the optimum kinetic parameters, we have solved the set of differential equations numerically by the technique of multivariate non-linear regression (Mult-NLR). Excellent agreement was obtained between calculated and experimental curves. © 1998 Elsevier Science B.V.

Keywords: Curing; DSC; Epoxy; Kinetics; Mechanism

1. Introduction

Thermosetting epoxy resins are widely used as adhesives, composites and laminates. The curing conditions strongly influence the intended mechanical, thermal and electrical properties. The optimization of the curing requires a reliable kinetic model of the consecutive and competitive reactions during this process. For that reason, the mechanism and kinetics have been intensively studied in the past. A comfortable, rapid and relevant experimental technique is DSC. Up to now, the kinetics of even low molecular model systems is not fully understood. The actual mechanism of the curing reaction is much more complicated than the very simple kinetic approximations frequently used. Using primary amines, agreement is mainly based on the following two main reactions:



$$\underset{O}{-CH{-}CH_2} + -NH_2 \xrightarrow{k_p} -\underset{OH}{CH}{-}CH_2{-}\underset{H}{N}-$$

$$\underset{O}{-CH{-}CH_2} + -\underset{OH}{CH}{-}CH_2{-}\underset{H}{N}- \xrightarrow{k_s} \left(-\underset{OH}{CH}{-}CH_2-\right)_2 N-$$

Side reactions such as homopolymerization of the epoxide, etherification of polyadduct hydroxyls and intramolecular cyclization of the polyadduct are possible, but they can usually be neglected. The kinetic

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model commonly employed was originally derived by Smith [1]. The corresponding reaction scheme (Eqs. (1)–(3)) is very simple if the following two assumptions are fulfilled:

1. Possible differences in the reactivity of primary and secondary amines can be neglected.
2. Intentionally added catalytic species and catalytic impurities are missing (highly purified components).

$$\mathrm{E} + \mathrm{OH} \overset{K}{\leftrightarrow} \mathrm{E}\cdots\mathrm{HO} \qquad (1)$$

$$\mathrm{E} + \mathrm{A} \overset{k_1}{\rightarrow} \mathrm{PA} + \mathrm{OH} \qquad (2)$$

$$\mathrm{E}\cdots\mathrm{HO} + \mathrm{A} \overset{k_2}{\rightarrow} \mathrm{PA} + 2\,\mathrm{OH} \qquad (3)$$

where E, A, PA and OH are the epoxide, the amine, the polyadduct and the catalytic hydroxyl groups of the polyadduct, respectively.

The epoxide is activated by hydrogen bonding in the pre-equilibrium (1). Reaction (2) is the uncatalyzed reaction in parallel with the autocatalyzed reaction (3). The rate-determining step is the formation of a cyclic termolecular transition state [2,3] via reaction (3). Its structure is shown in Fig. 1 on the left.

Using the degree of conversion α, the overall equation used most frequently for the kinetic evaluation of DSC curves of equimolar mixtures is written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (4)$$

where k_1 and k_2 are overall constants for the uncatalyzed and the autocatalyzed reaction.

According to the Smith mechanism, the exponents m and n are 1 and 2. The usual use of n and m as empirical fitting parameters increases the validity range of Eq. (4), but the connection with the chemistry of the process is lost.

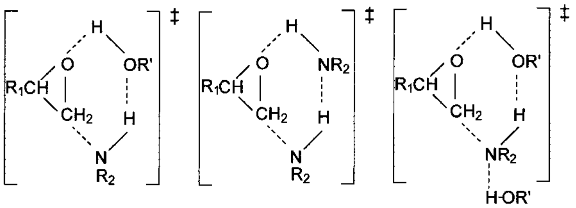


Fig. 1. The structure of the cyclic transition states for the autocatalyzed (on the left) and the uncatalyzed (middle) reaction between activated epoxide and amine. The possible transition state for the new additional route is shown on the right.

In a previous paper [4], we have calculated heat-flow rates, assuming the correctness of the Smith mechanism. Then, we have shown that the overall kinetic Eq. (4) is not the correct equivalent of this mechanism because the pre-equilibrium (1) is not taken into account correctly. Further, the usual evaluation by plotting the so-called reduced reaction rate $\mathrm{d}\alpha/\mathrm{d}t/(1-\alpha)^2$ vs. α is very problematic at high conversions. This results from the difficulty in distinguishing between signal and noisy baseline. The relative errors of the ever decreasing heat-flow rates increase strongly towards the (apparent) end of the reaction.

The present power of computer-aided evaluation provides a much better possibility to overcome the mentioned difficulties. The system of differential equations for an assumed and most probable mechanism is solved numerically. By using the Mult-NLR technique [5,6] the optimum kinetic parameters are obtained. Mult-NLR tries to describe several measurements (hence the notion multivariate), which are carried out under very different conditions (initial concentrations of the reactants, isothermal temperatures, scanning rates), by the same model. All measurements involved should be described by a single parameter set. A global solution is sought.

Even by use of this modern and advantageous technique, our experimental curves could not be modeled satisfactorily by the original Smith mechanism. This was our starting point, in which a better description of the experimental curves by introducing of empirical fitting parameters should be avoided from the start.

2. Experimental

DGEBA, PGE, aniline and DBED were used as model compounds. Except DGEBA (Epilox 514®, Leuna-Werke), all substances were supplied by Aldrich. After purification of the compounds by distillation or recrystallization, the water content was determined by Fischer titration. The reaction mixtures were filled into pans for volatile samples and kept up to the measurement in liquid nitrogen. The DSC apparatus was a Perkin–Elmer DSC 2, modified by

Table 1
Component concentrations (in mol l^{-1}) for the three examined model systems

Approximate stoichiometric epoxide/amine ratio	DGEBA	Aniline	PGE	Aniline	DGEBA	DBED
5 : 1	—	—	—	—	5.867	1.166
4 : 1	6.295	1.608	—	—	—	—
3 : 1	—	—	—	—	5.375	1.781
2 : 1	5.872	2.963	6.290	3.146	4.860	2.426
1 : 1	5.190	5.140	5.500	5.50	3.772	3.789
1 : 1.5	—	—	4.880	7.320	—	—
1 : 2	4.114	8.590	4.390	8.780	2.540	5.332
1 : 4	3.001	12.151	3.130	12.520	1.623	6.480
1 : 10	—	—	1.680	16.810	0.760	7.561

an equipment for program control and data sampling (ifa GmbH Ulm, Germany). Temperature calibration, heat calibration and heat-flow rate calibration were controlled weekly. Isothermal measurements of the DGEBA/aniline systems were made between 375 and 425 K, whereas the more reactive DGEBA/DBED mixtures were investigated between 330 and 390 K. The PGE/aniline system was investigated only at 400 K. The heating rates of dynamic scans were in the 1–10 K min^{-1} range. An adequate reaction model to be found must describe the reaction behavior by a single parameter set, independently of the epoxide/amine ratio. Therefore, we have strongly varied the composition of the reaction mixtures. Table 1 shows the compositions of all the investigated mixtures.

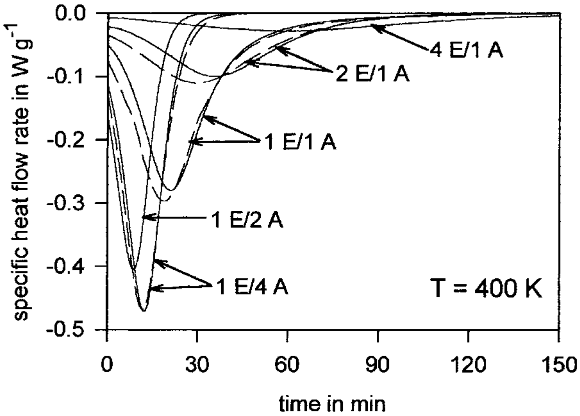


Fig. 2. Reaction isotherms for five DGEBA/aniline mixtures (solid lines) and three PGE/aniline mixtures (broken lines); E = epoxide, A = amine.

3. Results and discussion

Fig. 2 shows reaction isotherms for five DGEBA/aniline (solid lines) and three PGE/aniline (broken lines) mixtures at 400 K. The epoxide/amine ratio is comparable for corresponding curves of the two systems. The distinctive autocatalysis and the low contribution of the uncatalyzed reaction are typical of both aniline systems. An unintentional, catalyzed competitive reaction can be neglected in these high purified systems. Mixtures with excess aniline react much faster than equimolar mixtures or such ones with excess epoxide. The isotherms of the PGE/aniline system are very similar to those of the DGEBA/aniline system. This is a very important fact because the complete reaction proceeds in the low-molecular and low-viscous range in the former system. Therefore, one can exclude for both systems the often discussed recent possibility of a diffusion controlled reaction at high conversion degrees. The same holds for all the other reaction temperatures and all the used scan rates. Even the lowest reaction temperature of the DGEBA/aniline system was well above the final glass transition temperature (371 K), and the slowest scan rate of the dynamic measurements was still so fast that the increasing T_g never reached the present program temperature.

Fig. 3 shows some reaction isotherms for the DGEBA/DBED system. DBED is much more reactive than aniline. Therefore, the isothermal temperature is only

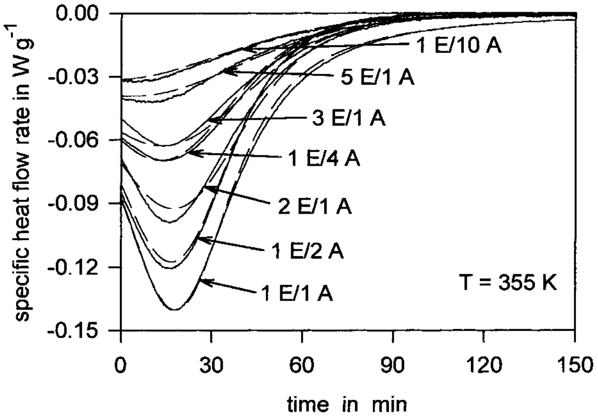


Fig. 3. Experimental (solid lines) and calculated (broken lines) reaction isotherms for some DGEBA/DBED mixtures; E = epoxide, A = amine.

355 K at comparable reaction times. Further differences are the pronounced uncatalyzed reaction, the lower contribution of the autocatalysis and the highest reaction rates of the equimolar mixture.

The average reaction enthalpies of the equimolar mixtures are in the usual range. We have found the following values: $-112.8\,\mathrm{kJ\,mol^{-1}}$ for the DGEBA/aniline system, $-112.4\,\mathrm{kJ\,mol^{-1}}$ for the PGE/aniline system and $-120.0\,\mathrm{kJ\,mol^{-1}}$ for the DGEBA/DBED system. Systems with epoxide or amine excess have somewhat higher values, but this shall not be discussed here. As already stated, the experimental curves, above all those with excess epoxide, cannot be successfully described by the Smith mechanism, even if one takes into account the different reactivities of primary and secondary amine hydrogens in the aniline system.

Obviously, the mechanism must be completed by a number of additional equilibria and reactions. Besides the E···OH complex, which is responsible, in the Smith mechanism, for the activation of the epoxide, A···OH, OH···OH (inter- and intramolecular), E···A and A···A complexes are known and possibly to be considered. A paper of Rozenberg [2] is a valuable source of information to this subject.

According to a few publications [2,7], the existence of A···A and OH···OH complexes can be neglected approximately in the kinetic model of polyaddition. Rozenberg [2] suggests a sort of compensation mechanism: The thermal effects of the formation and decomposition reactions (OH di-, tri- and tetramers) compensate for each other, independently of the composition of the reacting system. Further, the formation of A···A and OH···OH complexes decreases the concentration of the monomeric components, but the A···A and OH···OH species are probably more reactive [2], hence better catalysts [9]. Such a combination of positive and negative factors leads to a certain levelling off of the role of these complexes.

Concerning the E···A and the A···OH interactions, we have a very different situation. The E···A complexes are responsible for the initial rates of highly purified (no catalytic impurities, e.g. traces of water) reaction mixtures with low-reactivity aromatic amines. A simple nucleophilic addition to the epoxide ring is then impossible. The initial rate of such systems is proportional to $c_A^2 c_E$. Therefore, Enikolopiyan [8] suggests the preceding formation of an E···A complex because of the electrophilic attack of the epoxide oxygen by the amine hydrogen. In the next step, this complex reacts with another amine molecule. The sum of both reactions is the so-called noncatalytic reaction. This can be schematically written as:

$$\mathrm{A} + \mathrm{E} \overset{K}{\rightleftharpoons} \mathrm{A} \cdots \mathrm{E} \tag{5}$$

$$\mathrm{A} \cdots \mathrm{E} + \mathrm{A} \xrightarrow{k} \mathrm{Adduct} + \mathrm{OH} + \mathrm{A} \tag{6}$$

The structure of the transition state between E···A and A (Fig. 1, middle) corresponds completely to that of the corresponding state between E···OH and A. On the other hand, highly reactive amines like DBED react directly with the epoxide. The initial rate of mixtures with a different epoxide/amine ratio is proportional to $c_A c_E$. Then, the initial reaction is formulated as:

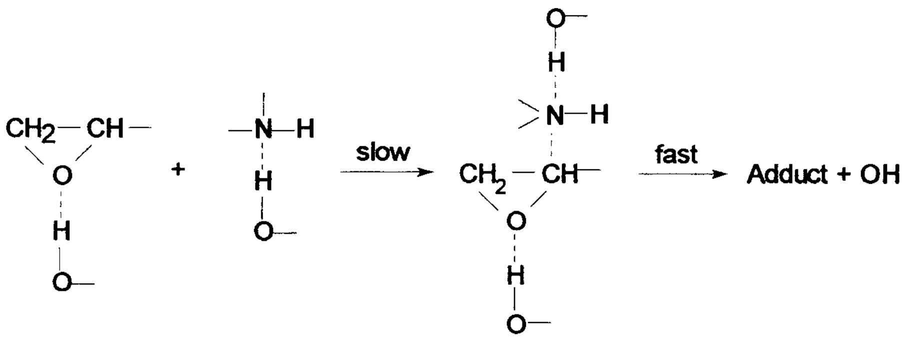
$$\mathrm{A} + \mathrm{E} \overset{K}{\rightleftharpoons} \mathrm{A} \cdots \mathrm{E} \tag{7}$$

$$\mathrm{A} \cdots \mathrm{E} \xrightarrow{k} \mathrm{Adduct} + \mathrm{OH} \tag{8}$$

The influence of the A···OH complexes is a matter controversy. Mika and Tanaka [10] simply exchange the roles of epoxide and amine in forming the ternary transition state. They assume the activation of the amine by a hydroxyl group and after that the interaction of A···OH with the epoxide. Enikolopiyan [8] retains the original Smith mechanism, but he additionally considers the existence of nonreactive A···OH complexes. Consequently, an autoinhibiting effect should be observed at higher conversion degrees, if the basicity of the formed secondary and tertiary amines is higher than that of the starting primary amines. Both modifications do not yield any improvement in modelling our experimental curves. Above all, according to Enikolopiyan, one should always find the slowest reaction rates in systems with excess amine. The very opposite effect was observed by us for the aniline systems (Fig. 2). Scarcely noticed was a proposal of Mijovic [11]. He suggests the following new reaction route, which acts as competitive reaction to the usual reaction between E···OH and A.

$$A + OH \overset{K}{\rightleftharpoons} A \cdots OH$$

$$E + OH \overset{K}{\rightleftharpoons} E \cdots OH$$



The possible structure of the transition state is shown on the right of Fig. 1. But the argument of Mijovic that this route is only active above a critical concentration of hydroxyl groups is not convincing. Of course, it does not reach a distinct extent until enough hydroxyl groups are formed. Nevertheless, a kinetic model must consider this new route during the entire reaction.

We therefore use, for the description of our systems, the following set of differential equations.

$$E + OH \overset{K_1}{\rightleftharpoons} EOH \tag{9}$$

$$P + OH \overset{K_2}{\rightleftharpoons} POH \tag{10}$$

$$S + OH \overset{K_3}{\rightleftharpoons} SOH \tag{11}$$

$$E + P \overset{K_4}{\rightleftharpoons} EP \tag{12}$$

$$EOH + P \xrightarrow{k_1} S + 2\,OH \tag{13}$$

$$EOH + POH \xrightarrow{k_2} S + 3\,OH \tag{14}$$

$$EOH + S \xrightarrow{k_3} T + 2\,OH \tag{15}$$

$$EOH + SOH \xrightarrow{k_4} T + 3\,OH \tag{16}$$

$$EP + P \xrightarrow{k_5} S + OH + P \tag{17}$$

$$ES \xrightarrow{k_5'} T + OH \tag{18}$$

where E, P, S and T are the epoxide, the primary, secondary and tertiary amines; EOH, POH and SOH are the corresponding hydroxyl complexes. Of course, using secondary amines as starting compounds, the equilibrium (10) and the reactions (13–14) are absent, and in the pre-equilibrium (12) the primary amine P must be replaced by the secondary amine S. Starting from primary amines, an ES complex and its reaction with P and S is conceivable, but this is just as meaningless as a reaction between EP and S!

The Eqs. (9)–(18) constitute the smallest possible and chemically relevant set of equilibria and reactions, which yields a consistent modelling of all investigated systems, including mixtures with higher epoxide concentrations. We have used simultaneously up to 24 data sets, differing in isothermal temperatures and

Table 2
Equilibrium constants and Arrhenius activation parameters for the systems DGEBA/aniline and DGEBA/DBED. The numbers for the equilibria and reactions correspond to those of the reaction scheme in the text

Equilibrium	$K/$ ($\mathrm{l\,mol^{-1}}$)		Reaction	$E_A/$ ($\mathrm{kJ\,mol^{-1}}$)		ln A/ ($\mathrm{l\,mol^{-1}\,s^{-1}}$)	
	aniline	DBED		aniline	DBED	aniline	DBED
10	0.70	0.71	14	55.7	—	10.52	—
11	0.38	—	15	44.7	—	8.15	—
12	0.21	0.41	16	56.3	50.4	8.85	10.29
13	0.055	0.28	17	42.7	40.2	6.79	5.83
			18/19	63.1	58.9	11.23	12.40

Table 3
Rate constants at 400 K

Reaction	$k/$ ($\mathrm{l\,mol^{-1}\,s^{-1}}$)		
	DGEBA/aniline	PGE/aniline	DGEBA/DBED
13	2.016×10^{-3}	1.806×10^{-3}	—
14	4.966×10^{-3}	3.128×10^{-3}	—
15	3.211×10^{-4}	3.013×10^{-3}	7.856×10^{-3}
16	2.377×10^{-3}	1.622×10^{-3}	1.929×10^{-3}
17 resp. 18	4.393×10^{-4}	4.656×10^{-3}	5.042×10^{-3}

compositions, to determine the optimal kinetic parameters of our model. The results are listed in the Tables 2 and 3. Of course, no activation parameters can be given for the PGE/aniline system. As expected from Fig. 2, the rate constants are very similar for the DGEBA/aniline and the PGE/aniline system (Table 3). If we assume the same equilibrium constants for the amine complexes of both systems, we obtain a somewhat higher equilibrium constant for the E$\cdots$OH complex ($K = 0.92\,\mathrm{l\,mol^{-1}}$) in the case of PGE. The correlation coefficient of all calculations is better than 0.999. To minimize the number of variation parameters, we have neglected the weak temperature dependence of the equilibrium constants. Further, we have restricted the variation limits of the equilibrium constants. Approximate starting values were obtained by comparison with published values. In the system DGEBA/aniline the calculated curves coincide with the experimental ones. This is true not only for the isothermal but also for the dynamic scans. Minor differences would not be recognizable on the scale of Fig. 2. Modelling the heat-flow rate curves for the DGEBA/DBED system, the agreement between experimental and calculated isotherms is not quite so good but still very satisfactory (Fig. 3). The activation energies decrease for both systems in the following order: uncatalyzed reaction > autocatalyzed reaction via $\mathrm{E+OH}$ > autocatalyzed reaction via $\mathrm{EOH+AOH}$. Of course, the amounts of reaction products formed via the different routes (Eqs. (13)–(18)) strongly depend on the used amine and the respective composition of the reaction mixture. Only 8–10% is formed via the noncatalytic reaction (Eqs. (12) and (17)) in the aniline system, whereas 25–35% is obtained via the corresponding route (Eqs. (12) and (18)) in the DBED system. The reaction route including the amine-hydroxyl complexes is quite unimportant in the DBED system (8–15%), whereas comparable amounts of adduct are produced in the aniline systems via the reactions 13 and 14 and thereafter via the reactions 15 and 16.

4. Conclusions

The suggested reaction scheme (Eqs. (9)–(18)) describes the curing reaction of the used model systems successfully. An inclusion of diffusion-controlled reaction steps at high conversion degrees is not necessay. The essential improvement in comparison with former models results from the consideration of an additional reaction route, first suggested by Mijovic [11]. Mult-NLR is an effective technique for the determination of the best model parameters. But a restriction must be made finally. If one takes into account the great number of model parameters (up to 4 equilibrium constants and up to 10 Arrhenius parameters) and the unavoidable errors of the experimental curves, the number of data sets (24), which can be evaluated by Mult-NLR at present simultaneously, is comparatively small. The minimum sum of the least squares is not situated in a deep valley but rather in a flat hollow. Further, more or less pronounced linear correlations exist between the parameters, for example between equilibrium constants and preexponential factors. Therefore, nearly just as good solutions are obtained for the system of differential equations if one equilibrium constant is maintained constant to a slightly different value. Clearly, only a reliable determination of the equilibrium constants by other techniques of instrumental analysis would improve this situation.

Acknowledgements

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