

## POSSIBILITIES OF APPROXIMATE DETERMINATION OF CURING TIME OF EPOXIDE RESINS WITH AROMATIC AMINES\*

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Extract percentage and values of glass transition temperature have been measured with respect to curing time of compositions of aromatic diamines with epoxide resins, and the times have been found which are necessary for obtaining practically constant measured quantities. Logarithms of the found curing times have been correlated with negative logarithms of the first dissociation constants ( $pK_{a1}$ ) of the diamines to give linear dependences the parameters of which agree with those of the straight lines found in correlations of kinetic data with  $pK_{a1}$  for the same reaction.

Addition reaction of primary and secondary amines with epoxy group is nucleophilic in its nature<sup>1</sup>, and it is generally faster when the electron density at amino nitrogen atom is higher and that at the attacked carbon atom of the epoxy group is lower. In the previous papers we tried to express quantitatively the effect of ring substituents of the aromatic amines on the velocity of their reaction with epoxy group using the correlations of logarithms of the rate constants with the Hammett  $\sigma$  constants,  $pK_a$  values of the amines, and electron density indices at the amino nitrogen atoms<sup>2-4</sup>. In all the cases linear dependences were found. The best correlation was that between the logarithms of the rate constants and  $pK_a$  values of the amines, being fulfilled also by *ortho*-substituted derivatives and having the minimum scattering of experimental points around the straight lines.

The aim of the present paper was to find whether the dependences obtained can be used for approximative estimation of curing time of epoxide resins with aromatic amines. For the curing we chose the aromatic diamines of the type  $H_2N-C_6H_4-X-C_6H_4-NH_2$  (where X is  $CH_2$ , S, SO,  $SO_2$ ) and 1,2- and 1,4-diaminobenzenes. For evaluation of the degree of cure of the compositions of the given diamines with epoxide resin we chose the temperature of glass transition, which is very sensitive in reflecting the degree of cure<sup>5</sup>, and the amount of the soluble portion in the cured systems, which was determined by extraction of samples with chloroform.

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## EXPERIMENTAL

**Reagents.** 4,4'-Diaminodiphenylmethane (m.p. 91–93°C), 1,2-diaminobenzene (m.p. 102 to 103°C), and 1,4-diaminobenzene (m.p. 141–142°C) were commercial chemicals and were purified by distillation or crystallization. 4,4'-Diaminodiphenyl sulphone (m.p. 176–177°C) was prepared by the method described in ref.<sup>6</sup>. 4,4'-Diaminophenyl sulphide (m.p. 107.5–109°C) and 4,4'-diaminodiphenyl sulphoxide (m.p. 175–177°C) were prepared by the method given in ref.<sup>3</sup>. The resin CHS Epoxy 15 was a product of Spolek pro chemickou a hutní výrobu Ústí n. Labem (Company for Chemical and Metallurgical Production, Ústí n. Labem), and its analysis gave 29.52% epoxy groups, 0.39% Cl and 1.24% OH groups.

**Gel time measurement.** The method described by Gough and Smith<sup>7</sup> was used: A thin-walled test tube, containing 0.05 to 0.1 g homogeneous mixture of curing agent and epoxide resin in stoichiometric ratio with respect to their functional groups, was placed into the vapour area in the flask equipped with thermometer, reflux condenser and a bored stopper. The mixture was stirred with a glass rod, and time was counted till the moment when the mixture began to climb up the rod.

**Curing of compositions.** Aromatic diamine was melted and the epoxide resin preheated at 110°C was added thereto, the amounts corresponding to the ratio of one epoxy group per one amino-hydrogen atom. The mixture was homogenized and transferred into a mould for casting plates which was then placed into drying oven at the chosen curing temperature. After the shortest chosen curing time the mould was taken out and the plate was cut into particles of 10 mm width. The particles were then further cured according to the chosen time programme. The time was counted from the moment of mixing of the both reaction components.

**Glass transition temperature measurement.** The method of linear dilatometry was chosen for the measurements. They were carried out with a thermomechanic analyzer Linseis with automatic registration of dilatation curves. The test bars 10 × 6 × 4 mm were tempered at the rate 2.5°C/min within –50°C and 250°C. The sample was fastened in a quartz enclosure and cooled with liquid nitrogen in a Dewar Flask. The dimension changes due to gradual increasing of temperature in an electrically heated oven were registered with a line recorder at a thousandfold magnification.

**Extraction of the cured compositions.** Samples of compositions of aromatic diamines and epoxide resin with various degrees of cure were cut into filings which were weighed (1.5 to 2 g) and placed into an extraction shell. The extraction was carried out with a Soxhlet apparatus and chloroform as solvent for 16 hours. Chloroform was distilled off *in vacuo*, and the residues were dried in a vacuum drying oven at 80 to 100°C for 8 hours. The samples were weighed, and the extracted portions were expressed in % by wt.

## RESULTS AND DISCUSSION

From our previous results<sup>2–4</sup> and from those of other authors<sup>8–10</sup> we came to a conclusion that the reactivity of aromatic amines to the epoxy group can be predicted from the quantum-chemical calculations as well as from the correlation of logarithms of rate constants with  $pK_a$  constants of the amines. Kinetic measurements of reactions of *ortho*-, *meta*-, and *para*-substituted anilines and aromatic diamines with epoxy compounds in ethanol or without solvent showed that the rate constants ratio of reactions of primary and secondary hydrogen atoms of amino group with

epoxy group ( $k_1/k_2$ ) was about  $4 \pm 1.5$  (ref.<sup>2-4</sup>) (except for few cases). Scattering of the values of this ratio is relatively large, but it must be taken into account that this value reflects the errors of determination of the both rate constants. Neither of the two studied series of aromatic amines showed any relation between the value of the ratio  $k_1/k_2$  and the quality of amine. Correlations of logarithms of the rate constants  $k_1$  and  $k_2$  of reactions of *ortho*-, *meta*-, and *para*-substituted anilines with *p*-tolyl-2,3-epoxypropyl ether with the Hammett  $\sigma$  constants gave practically the same values of slopes *viz.*  $-1.32$  and  $-1.27$ , respectively<sup>2</sup>. For these reasons we suppose that the reactivity ratio of primary and secondary amino-hydrogens towards epoxy group is practically constant for the amines studied. In the study of reaction of aromatic diamines with 2,2-bis(4-(2,3-epoxypropoxy)phenyl)propane<sup>4</sup> it was found that the reaction at 80°C is kinetically controlled up to 70% conversion, and at 120°C the diffusion-controlled region was found as high as above 80% conversion. Presuming that the ratio  $k_1/k_2$  is constant in the studied series of diamines and that the reaction is kinetically controlled up to high conversion degrees, we can expect that it will be possible to predict the curing times of compositions of aromatic amines and epoxide resins (having the stoichiometric ratio of amino to epoxy groups 1 : 2) from the found correlation dependences between kinetic quantities and  $pK_{a1}$  values.

So far we have carried out kinetic measurements with *p*-tolyl 2,3-epoxypropyl ether and 2,2-bis(4-(2,3-epoxypropoxy)phenyl)propane which are out of question as practical epoxy components. Now we have extended the kinetic experiments by the use of the resin CHS Epoxy 15 which has practical importance. Gel time (*G*)

TABLE I

Gel Times (*G*) of Mixtures of Aromatic Diamines with Epoxide Resin

*I* 4,4'-Diaminodiphenylmethane, *II* 4,4'-diaminodiphenyl sulphide, *III* 4,4'-diaminodiphenyl sulphoxide, *IV* 4,4'-diaminodiphenyl sulphone, *V* 1,2-diaminobenzene, *VI* 1,4-diaminobenzene.

Diamine	°C	<i>G</i> , min	Diamine	°C	<i>G</i> , min
<i>I</i>	79.5	66.5	<i>IV</i>	99.5	488
	99.5	31.0		116.5	288
	116.5	16.1	<i>V</i>	79.5	86.5
<i>II</i>	79.5	121.5		99.5	47.0
	99.5	58.5		116.5	26.0
	116.5	33.0	<i>VI</i>	79.5	20.2
<i>III</i>	79.5	325		99.5	9.10
	99.5	164		116.5	4.80
	116.5	93.5			

was chosen as a measure of reactivity of individual diamines. Table I gives gel times of mixtures of aromatic diamines with the resin at the boiling points of benzene (the measured value 79.5°C), water (99.5°C), and butanol (116.5°C). The values of logarithm of gel time were correlated with  $pK_{a1}$  values of the diamines. Linear dependences  $\log G = x pK_{a1} + Q$  were obtained the parameters of which are given in Table II. From the Table it is obvious that the slopes of the dependences studied are affected only slightly by reaction temperature, and the slope values found are comparable with the value 0.437 found in correlation of  $\log k_1$  with  $pK_{a1}$  of the reaction of aromatic diamines with 2,2-bis(4-(2,3-epoxypropoxy)phenyl)propane at 80°C.

For determination of degree of cure of compositions of the studied aromatic diamines with epoxide resin we chose the values of glass transition temperature (which is strongly dependent on the degree of cure even in the final phases<sup>5</sup>) and percentage of the non-cross-linked material which was measured by extraction of the cured samples with chloroform in a Soxhlet apparatus. The values of glass transition temperatures have only limited importance in our case and serve as a measure of curing of the system, because their determination is accompanied by additional curing, especially so in the cases of the less cured samples. Therefore, they are called  $T'_g$  in the present paper. The samples for extraction were cured in drying oven at 120°C, the time being prolonged till a constant amount of extract. The curing time of the samples for measurement of  $T'_g$  values was estimated from the values of the gel time calculated from the linear dependence  $\log G$  vs  $pK_{a1}$  of the reaction of aromatic diamines with epoxide resin at 99.5°C. The samples were heated in the drying oven at 100°C for the calculated gel time, and then they were cured at 150°C till the constant  $T'_g$  value. In the case of two chosen compositions this method was used for curing of the samples for extraction, too. The found values of amount of the extract (% by wt.) and the measured  $T'_g$  values were plotted in a graph wherefrom the minimum time was read for obtaining practically constant measured properties. Typical dependences are given in Figs 1 and 2. The resulting values are

TABLE II

Parameters of Dependences of Gel Times ( $G$ ) of Mixtures of Aromatic Diamines with Epoxide Resin on  $pK_{a1}$  of the Diamines

$\log G = x \cdot pK_{a1} + Q$ ;  $R$  is regression coefficient,  $s$  standard deviation.

$T, ^\circ\text{C}$	$x$	$Q$	$R$	$s$
79.5	-0.424	3.932	-0.9904	$\pm 0.0220$
99.5	-0.453	3.783	-0.9864	$\pm 0.0907$
116.5	-0.463	3.599	-0.9923	$\pm 0.0721$

given in Table III which also involves a comparison of the time values for curing of two systems (4,4'-diaminodiphenylmethane resp. 4,4'-diaminodiphenyl sulphone with epoxide resin) till a constant value of extract amount and till a constant value of  $T'_g$ . From the Table it is obvious that the curing times determined by the extraction method were shorter in the both cases than those found from  $T'_g$  measurements. The difference is obviously caused by that the values of glass transition temperatures

TABLE III

Results of Measurements of Degrees of Cure for Compositions of Aromatic Diamines with Epoxide Resin

For diamines *I* to *VI* see Table I.  $t_1$  the minimum curing time at 120°C necessary for obtaining constant value of extract,  $t_2$  the minimum curing time at 150°C for obtaining constant  $T'_g$  value,  $t_3$  the minimum time of additional curing at 150°C for obtaining constant value of extract.

Diamine	$t_1$ , min	$t_2$ , min	$t_3$ , min	$T'_{g,max}$ , °C
<i>I</i>	180	130	120	162.5
<i>II</i>	375	180	—	166
<i>III</i>	1 200	780	—	170
<i>IV</i>	3 860	1 320	1 100	186.5
<i>V</i>	300	130	—	150
<i>VI</i>	30	60	—	139

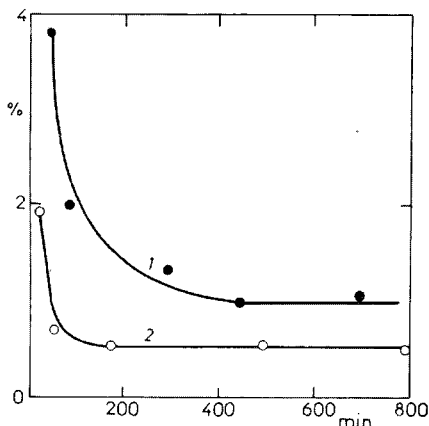


FIG. 1

Dependence of Extract on Curing Time at 120°C for Compositions of Epoxide Resin and 4,4'-Diaminodiphenylmethane (2) and 4,4'-Diaminodiphenyl Sulphide (1)

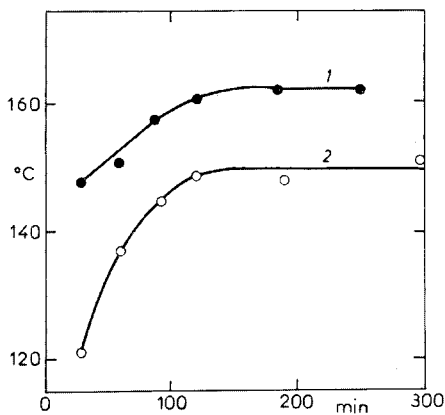


FIG. 2

Dependence of  $T'_g$  on Curing Time at 150°C for Compositions of Epoxide Resin with 4,4'-Diaminodiphenylmethane (2) and 1,2-Diaminobenzene (1)

are more sensitive in expressing the changes of degree of cure of the system than the value of extractable portion in the cured composition.

Plotting of logarithms of the times necessary for obtaining the minimum amount of extracts against negative logarithms of the first dissociation constants of the diamines gave a linear dependence  $\log t = -0.452 \text{ p}K_{a1} + 4.643$ , the regression coefficient being  $-0.9934$ . 1,4-Diaminobenzene, being rather deviated, was not involved in the calculation. The curing time of epoxide resin with this diamine is shorter than that calculated from the correlation  $\log t$  vs  $\text{p}K_{a1}$ . 1,2-Diaminobenzene is the most reactive out of the whole investigated series of diamines, and its reaction with epoxide resin is accompanied by considerable exothermic temperature increase. It is supposed that this is the reason of the deviation found. The slope  $-0.452$  of the straight line agrees well with the slope values found in correlation of logarithms of rate constants<sup>3</sup> and gel times of this reaction (Table II) with  $\text{p}K_{a1}$  values.

Logarithms of the times necessary for reaching the final  $T'_g$  value were plotted against  $\text{p}K_{a1}$  values, and, again, a linear dependence was obtained:  $\log t = -0.402 \text{ p}K_{a1} + 4.145$ ; the regression coefficient  $-0.9865$ . In this case the correlation was good inclusive of 1,4-diaminobenzene. The different behaviour of 1,4-diaminobenzene in the both correlations is probably due to different temperatures during curing. The samples for measurements of extraction were cured at  $120^\circ\text{C}$  for all the time, whereas those for  $T'_g$  determination were cured at  $100^\circ\text{C}$  till the calculated gel time. It seems likely that the latter curing method was accompanied by a smaller exothermic increase of the reaction temperature in the samples. The parameters of the straight line found are again, within experimental error, in accord with those of the linear dependences found in kinetic measurements.

From the measurements carried out in this work it can be deduced that it is possible to estimate approximately the curing time of epoxide resins with aromatic amines. Kinetic measurements of the reactions<sup>2-4</sup> showed that correlation of kinetic results with  $\text{p}K_a$  values is better for this purpose than correlation with the quantum-chemically calculated electron density indices at amine nitrogen atoms. The  $\text{p}K_a$  values are relatively well accessible, the scattering of experimental points around the straight lines being substantially smaller than that in correlations with the quantum chemical data, and some *ortho*-substituted derivatives correlate in this case, too. We also found<sup>2,3</sup> that the correlations of logarithms of rate constants of reactions of *ortho*-, *meta*-, and *para*-substituted anilines and aromatic diamines with *p*-tolyl 2,3-epoxypropyl ether in ethanol with  $\text{p}K_a$  values gave very similar parameters of the straight lines, wherefrom it can be deduced that the dependence is generally valid for aromatic amines provided their amino group is not hindered by some bulky substituent which would affect its reactivity towards epoxy group in a different way as compared with the reactivity towards the proton.

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