Study of Epoxy Compounds. Part I. Curing Reactions of Epoxy Resin and Acid Anhydride with Amine and Alcohol as Catalyst

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INTRODUCTION

The curing reaction between an epoxy resin and an acid anhydride with or without a catalyst has been studied: Fisch et al.[1,2] Wegler,[3] Dearborn et al.,[4,5] and Fischer[6] proposed the reaction mechanism with or without acid catalysts, and Shechter and Wynstra[7] studied a base-catalyzed reaction for the curing of epoxy resin.

These studies, however, were made with "model substances" such as phenyl glycidyl ether and acetic anhydride, and the proposed mechanisms of the curing reaction were based upon work involving few problems: almost no reaction orders were determined and the effects of amine, alcohol, or both were studied qualitatively only, not quantitatively nor kinetically.

This paper deals with kinetic studies of the curing reaction of epoxy resins and acid anhydrides, both commercial grade, and the effects of tertiary amines as catalysts and of alcohols as diluents on the curing reaction. The reaction was studied by direct determination of functional groups of reactants with chemical analysis.

EXPERIMENTAL

Reagents

The epoxy resins were Shell Chemical Company Epikote 828 (E-828) and Epikote 1001 (E-1001); acid anhydride was Allied Chemical and Dye Corporation hexahydrophthalic anhydride (HHPA).

Their physical and chemical properties are shown in Tables I and II.

TABLE I
Properties of Epoxy Resins

Resins	d_D^{25}		η_{25}(ps.)		Epoxy equiv., g./equiv.	
	Obsd.	Lit.	Obsd.	Lit.	Obsd.	Lit.
E-828	1.5708	1.573[8]	154	100-150[8]	191.3 ± 3.2	175-210[8,9]
E-1001	—	—	—	—	490.0 ± 6.2	425-550[8,9]

TABLE II
Properties of Hexahydrophthalic Anhydride

| | M.p., °C. | | Acidity, 10^{-3} equiv./g.[11] | | | |
| | | | Hydrolysis | | Esterification | |
Appearance	Obsd.	Lit.	Obsd.	Lit.[a]	Obsd.	Lit.[a]
White crystal	34.5–35.6	35–36[10]	12.8 ± 1.8	12.99	6.44 ± 0.51	6.495

[a] Calculated from the formula given.

Tertiary amines and alcohols as catalysts or diluents were all reagent grade and were used after distillation.

Procedure

An epoxy resin and HHPA were heated separately to the desired temperature and mixed, and to these were added suitable quantities of tertiary amines and/or alcohols as catalysts or diluents.

The time of adding the catalyst was recorded as "zero" at the reaction time, and was defined as the "gel point" when no aliquot parts of the reaction system dissolved in such solvents as pyridine, dimethylformamide, or dioxane (see the section on Results).

In the equimolecular reaction of epoxy resin and HHPA, it took about 10 hrs. at 100°C. to reach the gel state in the system E-828/HHPA and about 3.5 hrs. at 110°C. in the system E-1001/HHPA without a catalyst. Therefore one may disregard the time between the mixing of resin and HHPA and the adding of catalyst.

The aliquot parts of the reaction mixture were taken at convenient intervals and analyzed chemically as described below.

Analytical Methods

The epoxide and acid anhydride contents of the reaction system were determined by the pyridine–pyridinium chloride method[12] and the esterification method,[11] respectively. The acid anhydride determination gave a good analytical result with 0.31–0.67% error, independent of the epoxide and acid contents. On the other hand, the epoxide determination was affected by the epoxide and acid contents, and gave a 2–3% maximum error.

The determinations of epoxide and anhydride after gelation of the system were made with crushed samples and 80–100 mesh filters.

The extent of reaction, P, was obtained as:

$$P = (C_i - C_t)/C_i = 1 - C_t/C_i \qquad (2\text{-}1)$$

where C_t and C_i are the concentrations of reagents in the reaction system at the time of measurement and at initial time of reaction, respectively. The rate equation of the second-order reaction was obtained as:

$$P/(1 - P) = k_2 C_i t = k_2' t \qquad (k_2 C_i = k'_2) \qquad (2\text{-}2)$$

when the initial concentration of epoxide, C_t, was the same as that of HHPA.

The ratio of epoxy resin to HHPA and/or catalyst is the molar ratio in all cases given below.

RESULTS

Reaction Order

In the reaction of E-828 or E-1001 with HHPA at 70–140°C. with certain amines as catalyst, there were almost no differences in decreases of the concentration between epoxide and HHPA, as shown in Figure 1.
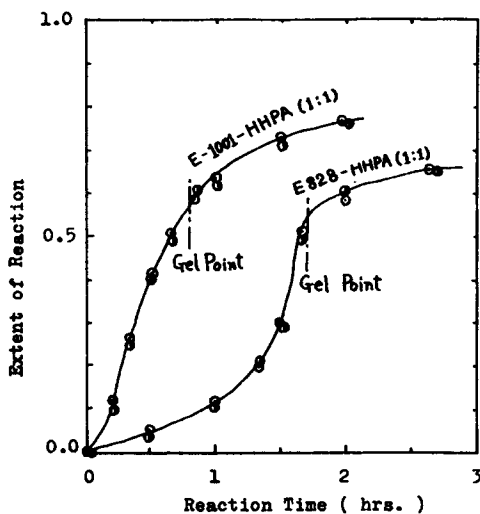

Fig. 1. Reaction between epoxy resins/HHPA and ca. 0.5% triethanolamine, at 100°C.: (⊙) epoxide; (◑) HHPA.
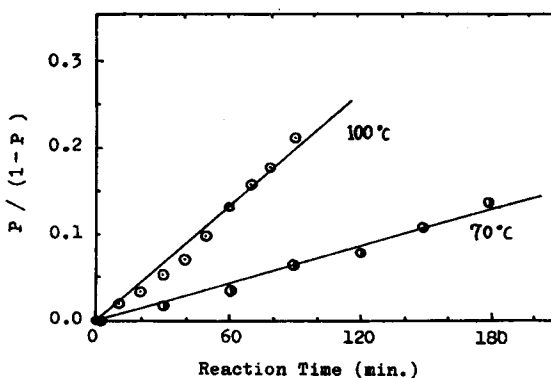
Fig. 2. Reaction of E-828/HHPA (1:1) with $N(CH_2CH_2OH)_3$ as catalyst; P is extent of reaction.
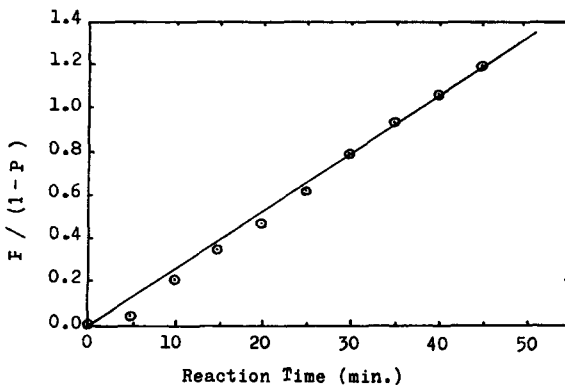
Fig. 3. Reaction of E-1001/HHPA (1:1) with $N(CH_2CH_2OH)_3$ as catalyst, at 100°C.

Figures 2 and 3 show that the curing reaction followed the second-order reaction, shown by eq. (2-2), in the systems E-828/HHPA (1:1) and E-1001/HHPA (1:1) at the temperatures given.   The rate equation of this curing reaction, then, is obtained as follows:

$$-d(\text{epoxide})/dt = -d(\text{acid})/dt$$

$$= K_A(\text{epoxide})(\text{acid}) \tag{3-1}$$

where K_A is the observed second-order rate constant containing the concentration of the catalyst.

Extent of Reaction at the Gel Time

As shown in Figures 4 and 5, the extents of reaction of epoxide and HHPA were nearly constant at the gel time in all cases, when the initial concentrations of epoxide and HHPA were fixed.
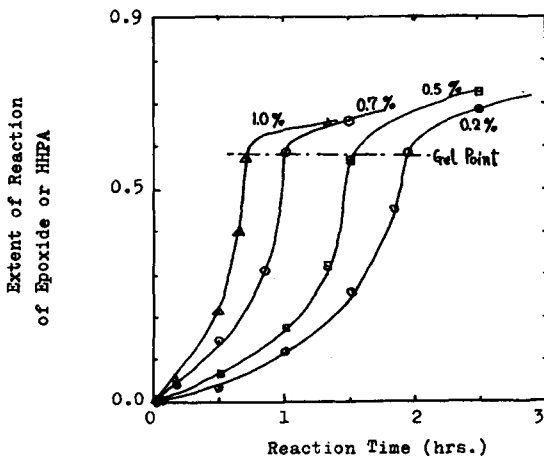
Fig. 4. Effect of triethanolamine on reaction of E-828/HHPA at 100°C. Amine concentration, 10^{-3} mole/g.: (△) 6.71; (○) 4.70; (□) 3.35; (◑) 1.34.
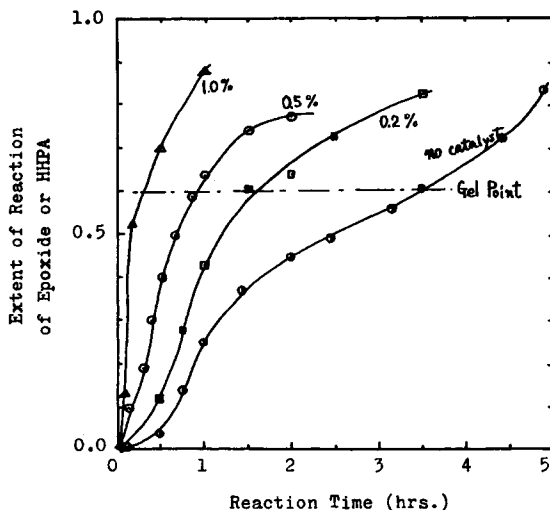
Fig. 5. Effect of triethanolamine on reaction of E-1001/HHPA (1:1), at 110°C. Amine concentration, 10^{-5} mole/g.: (△) 6.71; (⊙) 3.35; (▣) 1.34; (◐) none.

Effect of Amine Added as Catalyst

Effect of Concentration

Figures 4–6 show the effects of amine concentrations on the curing reaction of the system E-828/HHPA and E-1001/HHPA, and Figures 7 and 8 show those on the curing reaction of E-828/HHPA/methanol. There were almost no differences among the effects on these three systems within the limits of the conditions of this experiment.
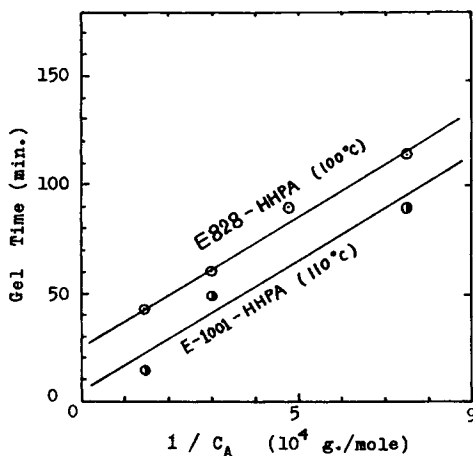
Fig. 6. Relation of gel time of reaction system of epoxy resin/HHPA (1:1) to initial concentration of triethanolamine, C_A.
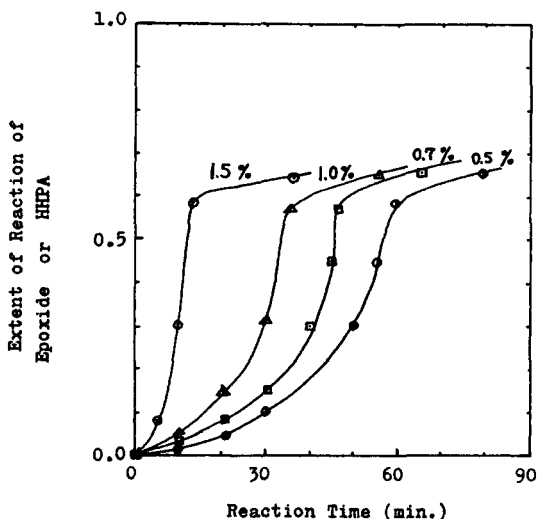
Fig. 7. Effect of triethanolamine on reaction of E-828/HHPA/methanol (1:1:0.01) at 90°C. Amine concentration, 10^{-5} mole/g.: (⊙) 10.47; (△) 6.98; (□) 4.78; (●) 3.49.
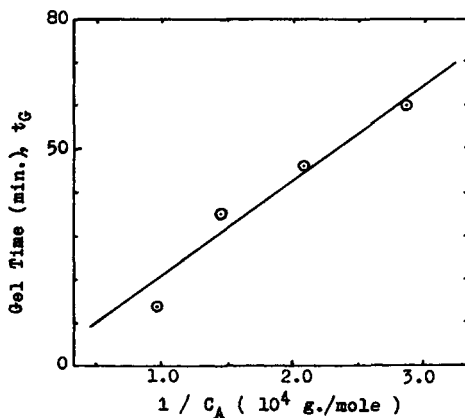

Fig. 8. Relation of gel time of E-828/HHPA/methanol (1:1:0.01) to initial concentration of triethanolamine.

Figures 6 and 8 show the following relation between initial concentration C_A of tertiary amine and gel time t_G:

$$C_A t_G = K \tag{3-2}$$

where K is a constant.

Effect of Various Amines

Figure 9 shows the catalytic effect of some amines on the reaction of E-828/HHPA/methanol (1:1:0.01). The effects may be assumed to
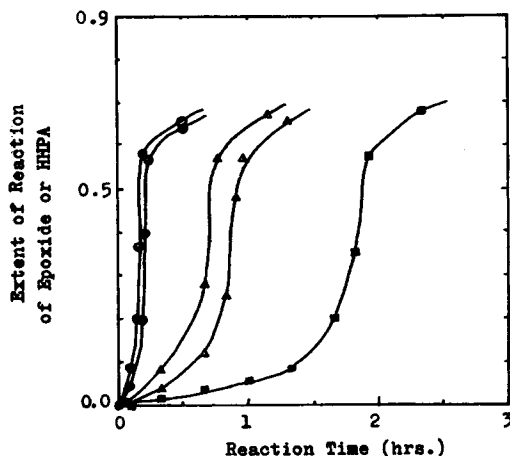
Fig. 9. Effect of amines (C_A = 3.49 × 10^{-5} mole/g.) on E-828/HHPA/methanol (1:1:0.01) at 90°C.: (⊙) benzyldimethylamine; (◑) pyridine; (△) triethylamine; (▲) triethanolamine; (▢) dimethylamine.

differ according to the distribution of electrons on the nitrogen atom of the tertiary amine.   This is shown in Table III.

TABLE III

Effect of Various Amines on Gel Time at 150°C. in the system E-828/HHPA (1:1)
(Catalyst concentration, 3.49 × 10^{-5} mole/g.)

Catalyst	Formula	Gel time, min.
Triethylamine	$N(C_2H_5)_3$	8
N-dimethylbenzylamine	$C_6H_5CH_2N(CH_3)_2$	2
Triethanolamine	$(C_2H_4OH)_3N$	10
N-dimethylaniline	$C_6H_5N(CH_3)_2$	22
Pyridine	⟨N⟩	3
Trimethylamine	$N(CH_3)_3$	6

Effect of Alcohol Added as Diluent

Effect of Concentration

Figure 10 shows the effect of the initial concentration of alcohol (mono alcohol) on the curing reaction of E-828/HHPA/triethanolamine (1:1: 0.012) at 100°C.

The same relation given by eq. (3-2) is obtained between the initial alcohol concentration C_A and the gel time t_G, as shown in Figure 11.   The effect of alcohol is not as great as that of amine (Tables IV and V).   When the initial concentration of alcohol was larger than 14.3 × 10^{-4} mole/g. the extent of reaction of acid anhydride was larger than that of epoxide and gelation did not occur.
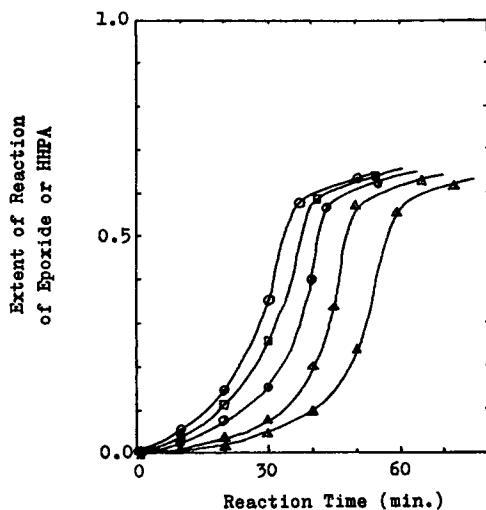
Fig. 10. Effect of concentration of butyl alcohol on E-828/HHPA/triethanolamine (1:1:0.012) at 100°C. Alcohol concentration, 10^{-4} mole/g.: (⊙) 2.85; (□) 1.99; (◑) 1.14; (△) 0.29; (▲) none.
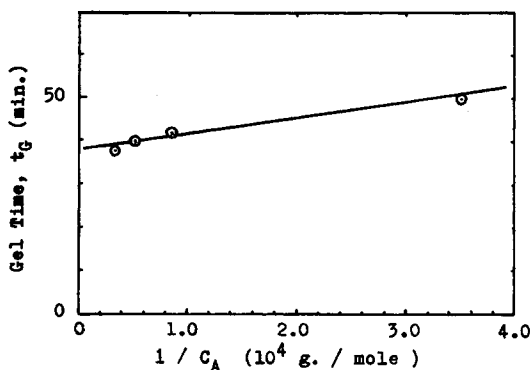

Fig. 11. Relation of gel time of E-828/HHPA/triethanolamine (1:1:0.012) to initial concentration of butyl alcohol at 100°C.

Effect of Various Alcohols

Figure 12 shows the catalytic effect of alcohol on the curing reaction of E-828/HHPA/triethanolamine (1:1:0.012) at 100°C., and Table V that on its gel times.

Effects of Reaction Temperature

Figure 13 and 14 show the reactions of E-828/HHPA and E-1001/HHPA with 0.5% triethanolamine at various temperatures. The apparent activation energies of these curing reactions were obtained as 14.1 and 14.4 kcal., respectively, from Figures 15 and 16, which show the temperature
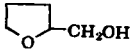
TABLE IV[16]
Effects of Various Amines on the Gel Time at 150°C.
(100 parts of E-828 and 60 parts of HHPA, by weight, with 1% of catalyst)

Catalyst	Gel time, min.
$C_6H_5CH(CH_3)N(CH_3)_2$	3
$(C_2H_5)_2NH$	20
$[(CH_3)_2CH]_2NH$	43
$(C_2H_4OH)_2NH$	38
$C_6H_5CH(CH_3)N(C_2H_4OH)_2$	41
$(CH_3)_2C(OH)NH_2$	164
$(C_2H_5)_3N$	5 (8)
$C_6H_5CH_2N(CH_3)_2$	2
$(C_2H_4OH)_3N$	7 (10)
$CH_3NH(C_2H_4OH)$	20
$(C_2H_4OH)NH_2$	129
$CH_3N(C_2H_4OH)_2$	3

TABLE V
Effect of Alcohols on Gel Time at 100°C.[a]

Alcohols	Gel time, min.
CH_3OH	35
n-C_4H_9OH	47
$(CH_3)_2C(CH_2OCH_3)OH$	51
$C_4H_9OCH_2CH_2OH$	54
$C_6H_5CH_2OH$	55
$C_8H_{17}OH$	66
C_2H_5OH	30
$CH_2(OH)CH_2OH$	68
$(CH_3)_2CHCH_2CH_2OH$	72
$CH_2(OH)CH(OH)CH_2OH$	89
(structure)—CH_2OH	51

[a] Concentration of alcohol was 0.285×10^{-4} equiv./g. in the system E-828/HHPA/triethanol amine (1:1:0.012).

dependence of the time it took the extent of reaction to reach a convenient value, such as 20, 30, or 40%. The apparent activation energies agreed with the value of 13.7 kcal./mole obtained from Figure 17, showing the temperature dependence of the time it took the viscosity to reach a convenient difference from its initial value.

DISCUSSION

Figure 1 shows almost no differences in conversion between the epoxides and acid anhydride within the conditions of this experiment, and implies the etherification reaction:
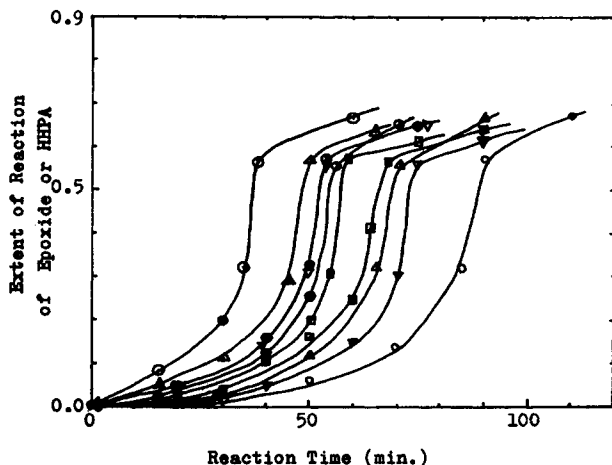
$$\overset{|}{\underset{|}{C}}HOH + O\!\!\diagdown\!\!\begin{array}{c}CH_2\\CH\\|\end{array} \rightarrow H\overset{|}{\underset{|}{C}}OCH_2CH(OH)- \qquad (4\text{-}1)$$
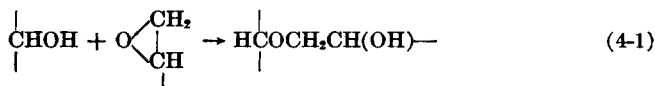
Fig. 12. Effect of alcohols (C_A = 0.285 × 10^{-4} mole/g.) on E-828/HHPA/trieth-anolamine (1:1:0.012) at 100°C.: (⊙) CH_3OH; (△) $n\text{-}C_4H_9OH$; (⊗) $(CH_3)_2C(OH)\text{-}CH_2COCH_3$; (▽) ⌐O⌐—$CH_2OH$; (◑) $C_4H_9OCH_2CH_2OH$; (□) $C_6H_5CH_2OH$; (▣) $C_8\text{-}H_{17}OH$; (▲) $(CH_2OH)_2$; (▼) $(CH_3)_2 CHCH_2CH_2OH$; (○) $CH_2(OH)CH(OH)CH_2OH$.
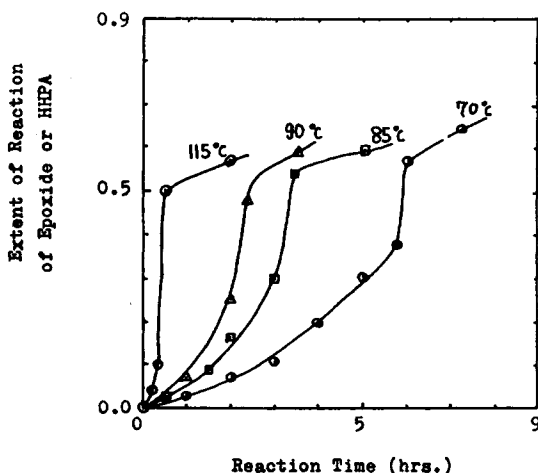

Fig. 13. Reaction of E-828/HHPA (1:1) with 0.5% triethanolamine at various temperatures.

This did not occur, even in E-1001/HHPA, which has an —OH group in its molecular structure.[9] This is consistent with Fischer's[4] result obtained from the study of the reaction between alyl glycidyl ether and phthalic anhydride at 70–100°C.

As shown in Figures 6 and 8 and by eq. (3-2), the curing reaction rate is proportional to the initial concentration C_A of amine added as catalyst in all systems of E-828/HHPA, of E-1001/HHPA having the secondary alcohol groups in the system, and of E-828/HHPA/methanol which con-

tains the primary alcohol groups.   The rate equation $-dx/dt$ (decreasing velocity of epoxide or anhydride) is obtained as follows:

$$-dx/dt = KC_A f(x) \qquad\qquad (4\text{-}2)$$

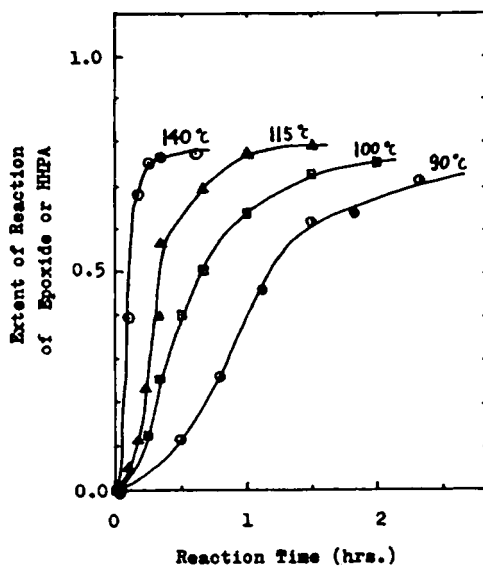where K is a constant, and this is consistent with Fischer's result [6]

Fig. 14. Reaction of F-1001/HHPA (1:1) with 0.5% triethanolamine at various temperatures.
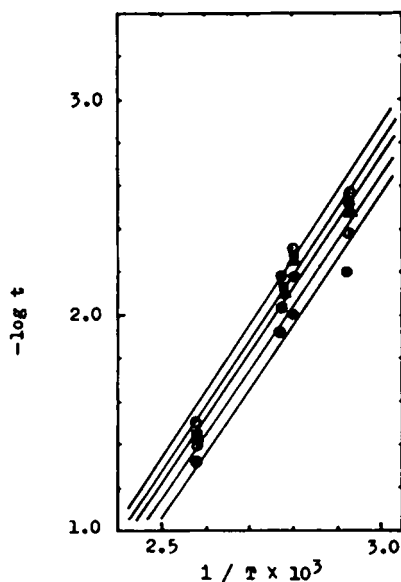

Fig. 15. Temperature dependence of reaction of E-828/HHPA (1:1) with 0.5% triethanolamine.   Conversion: (⊙) 55% (gel point); (□) 40%; (▲) 30%; (◑) 20%; (⊗) 10%. $E_A = 14.1$ kcal./mole.

The initial concentrations of epoxide and acid anhydride being a and b, respectively, $f(x)$ is obtained from the results of Figures 2 and 3, that is, eq. (3-1):

$$f(x) = (a - x)(b - x) \qquad (4\text{-}3)$$
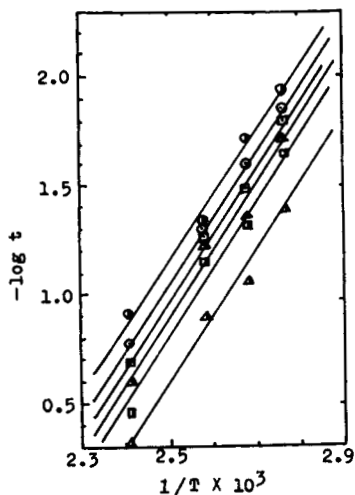
Fig. 16. Temperature dependence of reaction of E1001/HHPA (1:1) with 0.5% of Triethanolamine. Conversion: (◑) ca. 57% (gel point); (○) 50%; (□) 40%; (△) 30%; (◨) 20%; (▲) 10%. $E_A = 14.4$ kcal./mole.
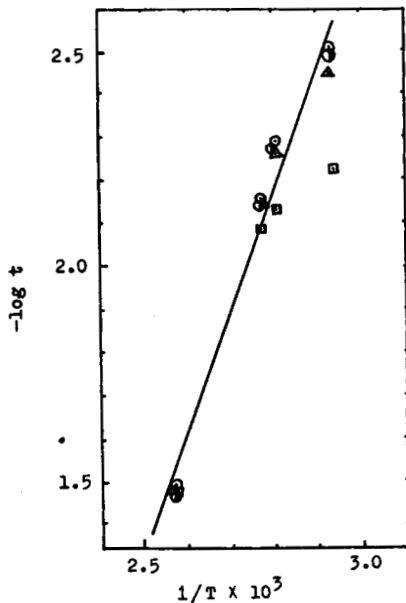

Fig. 17. Temperature dependence of time viscosity of E-828/HHPA (1:1)-triethanol-amine (0.5%) reaches convenient difference from initial value. Viscosity, centipoises: (○) 1500; (◑) 1000; (△) 500; (□) 100. $E_A = 13.7$ kcal./mole.

This disagrees with Fischer's result[6] in which the reaction is zero order in the system of alyl glycidyl ether/phthalic anhydride, with a tertiary amine, at 70–100°C.

Now, let us consider the following reactions:

(4-4)

(4-5)

(4-6)

(4-7)
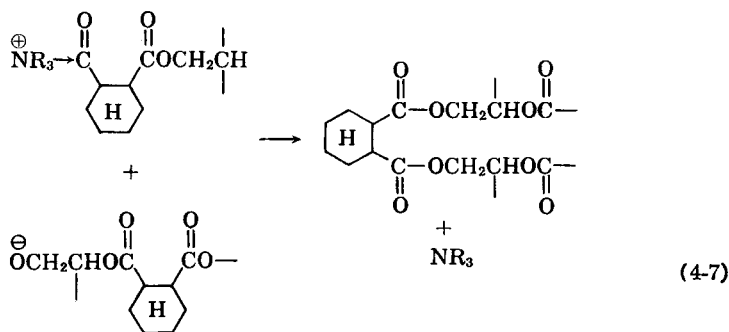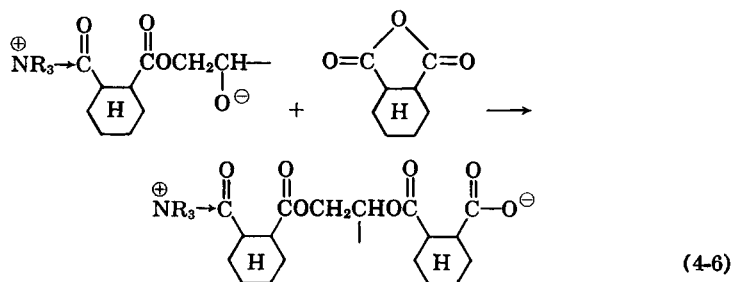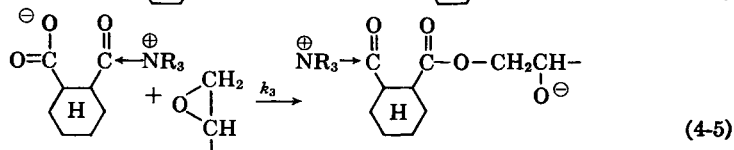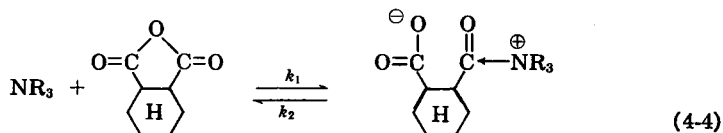
when C_A, C_B, C_D, and C_C are the concentrations of tertiary amine, acid anhydride, epoxide, and a conjugate base of tertiary amine with acid anhydride respectively, shown in the formula (4-4), the following equations are obtained:

$$dC_B/dt = -k_1 C_A C_B + k_2 C_C - k_3 C_C C_D \qquad (4\text{-}8)$$

$$dC_C/dt = k_1 C_A C_B - k_2 C_C - k_3 C_C C_D \qquad (4\text{-}9)$$

$$dC_D/dt = -k_3 C_C C_D \qquad (4\text{-}10)$$

Since $dC_C/dt = 0$ in the stationary state, we can obtain:

$$C_C = k_1 C_A C_B / (k_2 + k_3 C_D) \qquad (4\text{-}11)$$

with eq. (4-10); then, the equation of reaction rate v takes the form:

$$v = dC_D/dt = -k_1 k_3 C_A C_B C_D / (k_2 + k_3 C_D) \qquad (4\text{-}12)$$

If $k_1 > k_2 \gg k_3$, we can obtain:
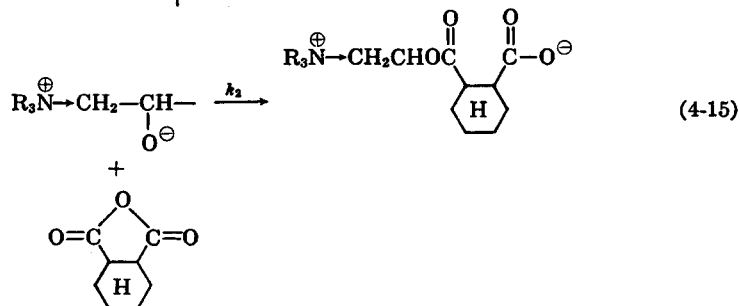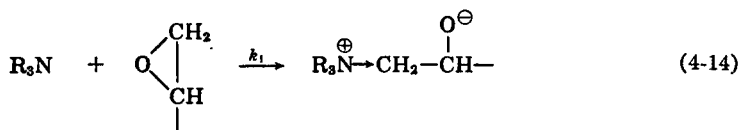
$$v = -(k_1 k_3 / k_2) C_A C_B C_D \qquad (4\text{-}13)$$

and eq. (4-13) explains more reasonably the results of Figures 2, 3, 6, and 8, and is consistent with the experimental equations of reaction rate, eqs. (3-1) and (4-2).

The following reactions, which are assumed to occur in these cures, may be ignored within these experimental conditions:

$$(4\text{-}14)$$

$$(4\text{-}15)$$

If the curing reaction follows eqs. (4-14) and (4-15), the reaction rate can be shown as:

$$v = dC_D/dt = -k_1 C_A C_D \qquad k_1 < k_2 \qquad (4\text{-}16)$$

$$v = dC_B/dt = -k_2 C_A C_B \qquad k_1 > k_2 \qquad (4\text{-}17)$$

and therefore disagrees with eq. (3-1) obtained from Figures 2 and 3.

The catalytic effects of amines depend upon the nucleophilic properties, that is, the basicities of amines, whether or not they are shown in eqs. (4-4) or (4-14) (they may be ignored in these cases).

Parker and Isaacs give the following equation:[13]

$$(\log k - \log k_0)/\sigma^* = \rho_p + \rho_s E_s / \sigma^* \qquad (4\text{-}18)$$

where k_0 and k are the rate constants for the reactions of a given compound and of one of its substituted derivatives, σ^* is the polar substituent constant characteristic of the substituent, E_s the steric substituent constant, ρ_p the polar reaction constant, and ρ_s a measure of the susceptibility of the reaction to the steric effects of substituents.
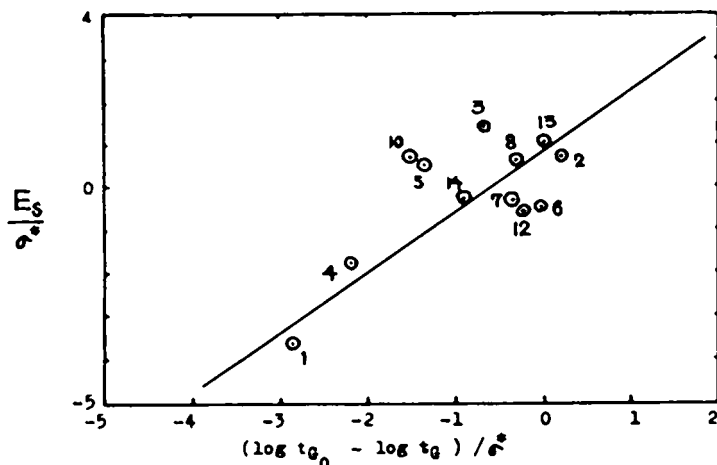
Fig. 18. Plot of $(\log t_{G_0} - \log t_G)/\sigma^*$ versus E_s/σ^* for reactions of E-828/HHPA with various amines as catalysts. Parent amine, NR_3, is trimethylamine, $N(CH_3)_3$, for which σ^* and E_s are both zero. Substituent groups, R, of amine NR_3 are as follows: (1) $C_6H_5CH(CH_3)$— and $(CH_3)_2$—; (2) $(C_2H_5)_2$—; (3) (C_2H_5)— and H—; (4) $C_6H_5CH_2$— and $(CH_3)_2$—; (5) $[(CH_3)_2CH]_2$— and H—; (6) $(C_2H_4OH)_2$—; (7) $(C_2H_4OH)_2$— and H—; (8) C_2H_4OH—, H—, and CH_3—; (9) $C_6H_5CH(CH_3)$— and $(C_2H_4OH)_2$—; (10) (C_2H_4OH)— and H_2—; (11) H_2— and $(CH_3)_2COH$—; (12) CH_3— and $(C_2H_4OH)_2$—; (13) $(CH_3)_2$—; (14) C_6H_5— and $(CH_3)_2$—. $\rho_p = -0.57$, $\rho_s = 0.71$.

Since $\log k - \log k_0$ is replaced by $\log t_{G_0} - \log t_G$ in these cases, as shown below, in Figure 18 $(\log t_{G_0} - \log t_G)/\sigma^*$ is plotted against E_s/σ^* for the curing reactions of epoxy resins and HHPA with various amines as catalysts at 150°C. (see Tables III and IV).

The rate equation of the second-order reaction given by eq. (4-2) may be rewritten as:

$$1/(a - b) \log[(a - x)/(b - x)](b/a) = k_2 C_A t \qquad (4\text{-}19)$$

and $1/[C_A(a - b)] \log [(a - x)/(b - x)](b/a) = K$ in the gel point t_G, eq. (4-19) becomes:

$$k_2 = K/t_G \qquad \text{at } t_G \qquad (4\text{-}20)$$

and $\log k - \log k_0 = \log t_{G_0} - \log t_G$.

The constants E_s and σ^* were given the values shown in the literature.[15]

The best straight line was found by the least-squares method and, from intercept and slope, ρ_p and ρ_s are found to be -0.57 and 0.71, respectively. The fit is certainly much better than that obtained by plotting $\log t_G$ against σ^* according to the simplified form of the Taft[14,15] equation. The fact that ρ_p is negative indicates that electron-repelling substituents of NR_3 increase the curing rate, as shown by eq. (4-12).

Figure 10 implies that the —OH group has an effect on the curing reaction of the epoxy resin with the acid anhydride, and Figure 11 shows that

the reaction rate is proportional to the concentration of alcohol and that the alcohol is not as effective as the amine.

The equation of reaction rate in the system of epoxide, acid anhydride, and alcohol, therefore, may be shown by eqs. (3-2) and (4-2) to be the same as that in the system of epoxide, acid anhydride, and amine.

Now the following elementary reactions being assumed to occur,

$$(4\text{-}21)$$

$$(4\text{-}22)$$
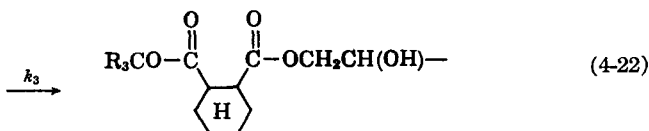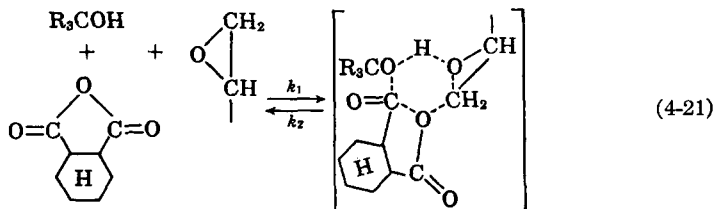
and C_A, C_B, C_D, and C_C being the concentrations of alcohol, acid anhydride, epoxide and activated complex of these three reagents, the following equations are obtained:

$$dC_B/dt = dC_D/dt = -k_1 C_A C_B C_D + k_2 C_C \qquad (4\text{-}23)$$

$$dC_C/dt = k_1 C_A C_B C_D - k_2 C_C - k_3 C_C \qquad (4\text{-}24)$$
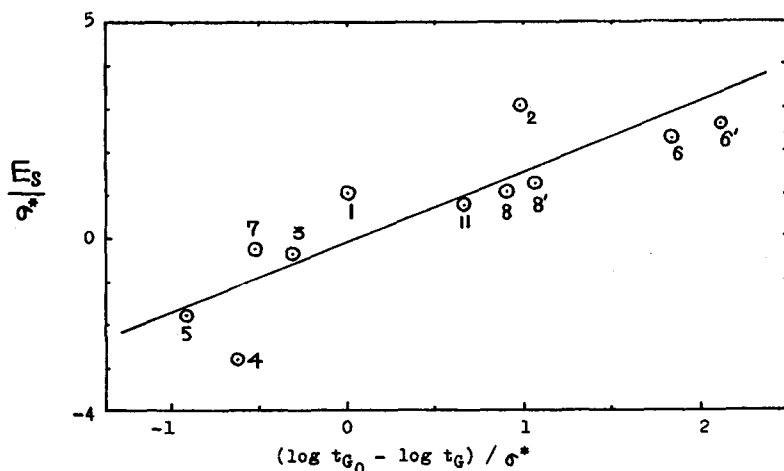
Fig. 19. Plot of $(\log t_{G_0} - \log t_G)/\sigma^*$ versus E_s/σ^* for reactions of E-828/HHPA (1:1) with various alcohols as catalysts. Parent alcohol, ROH, is methanol, CH_3OH, for which σ^* and E_s are both zero. Substituent groups, R, of alcohol, ROH, are as follows: (1) CH_3—; (2) n-C_4H_9—; (3) $(CH_3)_2C(CH_3—OCH_2)$—; (4) $C_4H_9OCH_2CH_2$—; (5) $C_6H_5CH_2$—; (6) C_8H_{17}—; (7) $CH_2(OH)CH_2$—; (8) $(CH_3)_2CHCH_2CH_2$—; (9) $CH_2(OH)CH(OH)$—; (10)⌐⌐—CH_2—; (11) C_2H_5—. $\rho_p = 0.063$, $\rho_s = 0.63$.

Since $dC_C/dt = 0$ in the stationary state, we obtain:

$$C_C = k_1 C_A C_B C_D/(k_2 + k_3) \qquad (4\text{-}25)$$

from eq. (4-23); then, the equation of reaction rate v takes the form of:

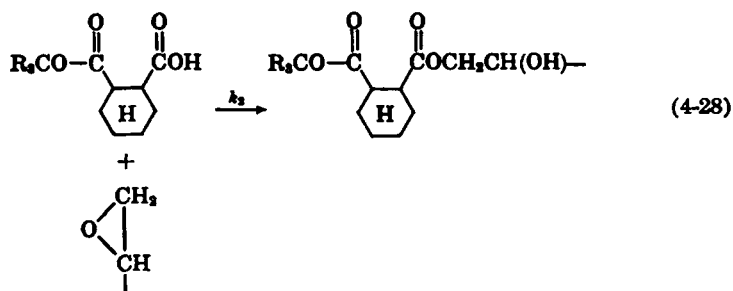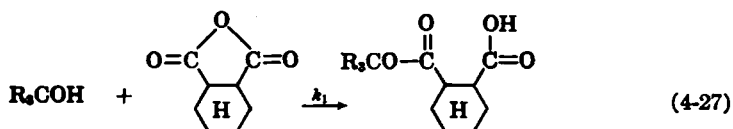$$v = dC_B/dt = dC_D/dt = -k_1 k_3 C_A C_B C_D/(k_2 + k_3) \qquad (4\text{-}26)$$

and eq. (4-26) explains more reasonably the results of Figure 11 and is consistent with the experimental equations (3-1) and (4-2). This result disagrees with Fischer's.

The following reactions are assumed to occur in these curing reactions:

$$(4\text{-}27)$$

$$(4\text{-}28)$$

The reaction rate obtained from eq. (4-16) or (4-17) disagrees with the experimental equations (3-1) and (4-2) and cannot explain the result in Figure 11.

The catalytic effect of alcohol being given by eq. (4-21), may depend on the activity of the hydrogen atom of alcohol, the —OH group.

In Figure 19, $(\log t_{G_a} - \log t_G)/\sigma^*$ is plotted against E_a/σ^* for the curing reactions of epoxy resins and HHPA with various alcohols as catalysts at 100°C. (see Table V). The best straight line has been found in the case of amines and, from intercept and slope, ρ_D and ρ_s are found to be +0.063 and +0.63, respectively. The fact that ρ_D is positive indicates that electron-withdrawing substituents increase the rate, as shown in Table V.

The results of Figures 18 and 19 supported better the proposed curing mechanisms of the eqs. (4-4) to (4-7) and (4-21) to (4-22).

References

1. Fisch, W., and W. Hofmann, *J. Polymer Sci.*, **12**, 497 (1954).
2. Fisch, W., et al., *J. Appl. Chem.*, **6**, Oct., 429 (1956).
3. Wegler, R., *Angew. Chem.*, **67**, 587 (1955).
4. Dearborn, E. C., et al., *J. Polymer Sci.*, **16**, 201 (1955).
5. Dearborn, E. C., et al., *Ind. & Eng. Chem.*, **45**, 2715 (1954).
6. Fischer, R. F., *J. Polymer Sci.*, **44**, 155 (1960).

7. Shechter, L., and J. Wynstra, *Ind. & Eng. Chem.*, **48**, 86 (1956).

8. Shell Chemical Corporation, *Tech. Bull.*, *Epikote Resins*, *RES:59: 12*, p. 3.

9. Lee, H., and K. Neville, *Epoxy Resins*, McGraw-Hill, New York, 1957, p. 20.

10. Allied Chemical & Dye Corporation, *Tech. Bull.*, *1-2, Hexahydro Phthalic Anhydride*.

11. Hammond, C. W., *Organic Analysis*, Vol. 3, Interscience, New York–London, 1956, p. 97.

12. Jungnickel, J. L., et al., *Organic Analysis*, Vol. 1, Interscience, New York–London, 1953, p. 136.

13. Parker, R. E., and N. S. Isaacs, *Chem. Rev.*, **59**, No. 4, 737 (1959).

14. Taft, R. W., *J. Am. Chem. Soc.*, **74**, 3120 (1952).

15. Taft, R. W., *Steric Effect in Organic Chemistry*, M. S. Newman, Ed., Wiley, New York, 1956, p. 556.

16. Cressy, K., et al., paper presented at the Atlantic City Meeting, Vol. 9, No. 2, *Paper 30*, September 1959.

Synopsis

The curing reaction of an epoxy resin and acid anhydride with an amine and/or alcohol was studied kinetically. No etherification reaction occurred at 70–140°C. and the initial reaction rate was proportional to the concentration of epoxide, acid anhydride, and catalyst (tertiary amine or alcohol). The apparent activation energies of the reaction in two systems of epoxy resin–hexahydrophthalic anhydride/triethanolamine (0.5 wt. %) were obtained as 14.1 and 14.4 kcal./mole. The effects of the substitution R of the tertiary amine NR_3 or alcohol R_3COH as catalyst on the curing reaction of the epoxy resin and acid anhydride were studied. The polar reaction constant ρ_p for amines, obtained negatively, indicates that electron-repelling substituents of NR_3 increase the curing rate; ρ_p for alcohols, obtained positively, indicates that electron-withdrawing substituents of R_3COH increase the rate of curing reaction. These results supported the proposed curing mechanism better.

Résumé

La réaction de vulcanisation entre la résine époxyde et un anhydride en présence d'amine et/ou d'alcool a été étudiée au point de vue cinétique en faisant usage de résines époxydes commerciales et d'anhydride. Aucune réaction d'éthérification ne s'est produite entre 70 et 190°C et la vitesse initiale de réaction est proportionnelle à la concentration d'époxyde, d'anhydride et de catalyseur tel qu'une amine tertiaire ou un alcool. Les énergies apparentes d'activation de la réaction dans deux systèmes résine époxide/anhydride hexahydrophtalique/triéthanol amine (0.5% en poids) ont été respectivement de 14,1 et 14,4 Kcal. On a étudié les effets du substituant R de l'amine tertiaire NR_3 ou de l'alcool R_3COH comme catalyseur sur la réaction de vulcanisation de la résine époxyde et de l'anhydride. La constante de polarité de la réaction ρ_p, négative dans le cas des amines, montre que les substituants électronégatifs de NR_3 augmente la vitesse de vulcanisation. ρ_p pour les alcools est postive et montre que les substituants électropositifs de R_3COH augmentent la vitesse de la réaction de vulcanisation. Ces résultats rendent plausible le mécanisme de vulcanisation proposé.

Zusammenfassung

Die Härtungsreaktion zwischen einem Epoxyharz und Säureanhydrid mit einem Amin oder Alkohol wurde kinetisch an handelsüblichen Epoxyharzen und Säureanhydriden untersucht. Bei 70–140°C. trat keine Verätherungsreaktion auf und die Anfangsgeschwindigkeit war der Konzentration von Epoxyd, Säureanhydrid und Katalysator, wie tertiäres Amin und Alkohol, proportional. Die scheinbare Aktivierungsenergie der Reaktion in den beiden Systemen des Epoxyharz–hexahydrophthal-

isches Anhydrid/Triäthanolamin (0,5 Gew. %) wurde zu 14,1 bzw. 14,4 kcal./mole bestimmt. Der Einfluss der Substituenten R des tertiären Amins NR_3 oder Alkohols R_3COH auf ihre Wirkung als Katalysator der Härtungsreaktion des Epoxyharzes und Säureanhydrids wurde untersucht. Die polare Reaktionskonstante, ρ_p, die für Amine einen negativen Wert besitzt, zeigt, dass elektronen-abstossende Substituenten von NR_3 die Härtungsgeschwindigkeit erhöhen. Für Alkohole ergab sich ρ_p positiv, was zeigt, dass elektronen-entziehende Substituenten von R_3COH die Geschwindigkeit der Härtungsreaktion erhöhen. Diese Ergebnisse bilden eine Stütze für den vorgeschlagenen Härtungsmechanismus.