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DETERMINATION OF CURE TIMES AND ACTIVATION ENERGIES OF ONE-CONTAINER EPOXY RESIN SYSTEMS BY ISOTHERMAL DSC *

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ABSTRACT

Cure times and activation energies of one-container epoxy resin systems were determined using two isothermal techniques on a DSC. Cure times were found to agree well with those determined by other methods. Activation energies of Bisphenol-based epoxy resins cured with dicy (dicyanodiamide) and anhydrides were found to agree with values reported in the literature. The effect of catalysis on the activation energy is discussed.

INTRODUCTION

This paper describes the use of DSC instrumentation operated in the isothermal mode to study cures of one-container epoxy resin systems. Such systems have the hardener mixed with the epoxy resin during manufacture; the resulting system is stable at ambient temperatures. One such curing agent, dicy (dicyanodiamide, cyanoguanidine) owes its latency to the fact that it is insoluble in liquid epoxy resin systems except at elevated temperatures. Other commercial products in the form of powders or flexible films are based on solid or partially reacted epoxy resins and hardeners which attain miscibility in the molten state. Systems of the latter type may be cured with dicy, solid anhydrides, or solid amines.

Neither reaction mechanisms nor reaction kinetics will be discussed in detail here, as these aspects of epoxy curing reactions have been well documented in the literature. Lee and Neville [1] give a comprehensive summary of the reactions of the epoxy group with functional groups found in various hardeners. The kinetics of epoxy curing reactions have been discussed in detail by Prime [2], Sacher [3], and Yevutushenko et al. [4]. This work deals rather with the more practical question of determining the time needed at a given temperature for essentially complete cure, and the determination of the activation energy from the temperature dependence of the cure time.

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Several methods for determining the cure time are available. ASTM D-1144 [5], which involves curing a bonded specimen at a given temperature for various times and constructing a plot of bond strength against exposure time, has been widely used in the adhesive industry. One could examine the change in any one of a number of properties, T_g [6], dynamic mechanical properties [7,8], electrical properties [4], etc., as a function of cure history. Several workers have utilized isothermal DSC as a technique for determining activation energies [9—13]. Gilham et al. [6] have used measurements of gel times and vitrification times at various temperatures to compute activation energies.

In this study, isothermal DSC was used to measure cure times at various temperatures. The activation energies were computed from the slopes of Arrhenius-type plots of log cure time vs. inverse temperature. It must be remembered that this slope is the negative of that obtained from plotting the rate constants, and that the Arrhenius pre-exponential factor cannot be obtained from the intercept.

EXPERIMENTAL

Epoxy resins used in this study were commercially available DGEBA (diglycidyl ether of Bisphenol-A) based resins. For convenience, only the average equivalent weights, as determined according to ASTM D-1652 [14], are reported here. Solid epoxy resins and hardeners were ground to a particle size of less than 125 μm before formulating.

Cure times were determined using a DuPont 990 thermal analysis system with a DSC cell, and a Perkin—Elmer DSC-II. Two techniques were evaluated; the first, described by Fava [9], involves insertion of the sample at ambient temperature, programming as rapidly as possible to the measurement temperature, and operating isothermally, following the DSC output as a function of time. The second method, described by Sourour and Kamal [10], involves pre-heating the DSC to the temperature of interest, starting the time base scan, and loading the sample into the cell as rapidly as possible.

Figure 1 illustrates a typical trace obtained by the Sourour method. At A, the DSC cell was opened and the sample inserted. At B, the sample side of the cell has reached the isothermal value and the sample commences curing. Curing is essentially complete at C, and the cure time is taken as $t(\mathrm{C} - \mathrm{B})$, and will henceforth be referred to as t_c.

Thermograms obtained by the Fava method are qualitatively similar except that the induction time $t(\mathrm{B} - \mathrm{A})$ is much greater, although no significant differences were observed between results obtained by either method on either of the stated instruments for cure times in the order of 10—20 min. For very fast reactions, the longer induction time associated with the Fava method may introduce some error if the DuPont instrument is used. For this reason, all data reported here were obtained using the Sourour method, and were generated on both systems.

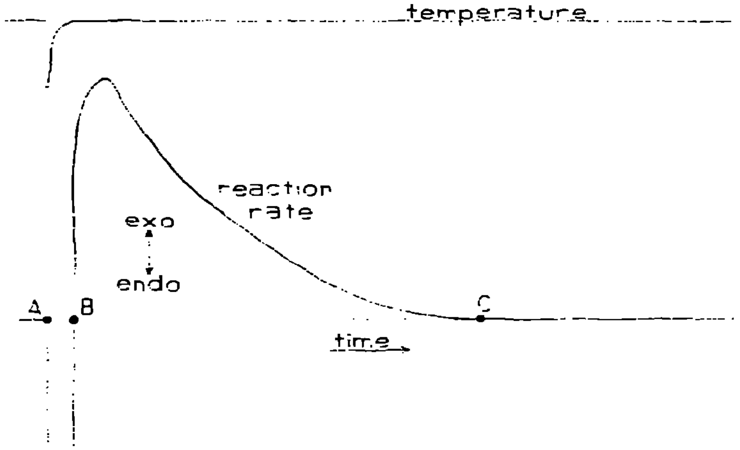

Fig. 1. Typical thermogram of isothermal cure by the Sourour method (pre-heated DSC cell). Sample was loaded at point A.

RESULTS AND DISCUSSION

If, as was postulated by Fava [9], any changes in the curing mechanism with temperature do not affect the overall reaction order, Arrhenius plots of log t_c vs. inverse cure temperature will be linear, as is shown in Fig. 2 for two epoxy-based powder coatings of unknown composition. For this data, relative standard error was about 3% for each point, and the correlation coefficient for the linear regression was 0.997. Activation energies, calculated from the slopes of the Arrhenius plots, were 12.0 kcal mol^{-1} for sample A and 10.8 kcal mol^{-1} for sample H.

The data in Table 1 give an indication of the reproducibility of the meth-

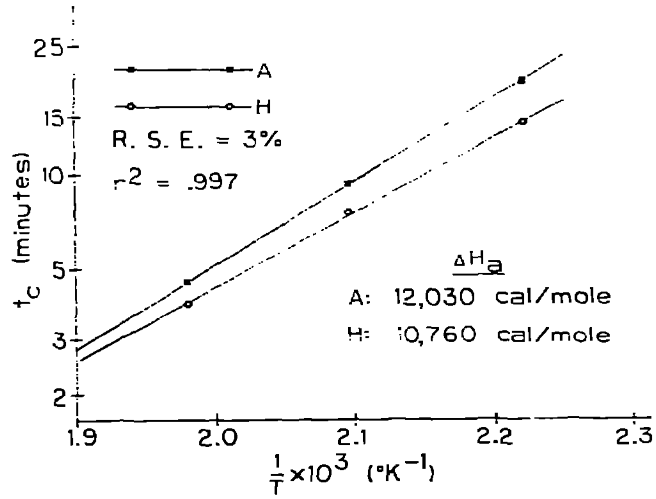

Fig. 2. Arrhenius plot of cure time data on two powder epoxy systems of unknown composition.

TABLE 1

Comparison of results on samples manufactured and tested on widely separated dates shows the reproducability of the method

Sample	ΔH_a (kcal mol^{-1})	Cure times, t_c (min)		
		400°F	350°F	300°F
1590	16.9	5.6	16.3	57
1591	16.7	5.5	15.8	55
1592	16.8	5.6	16.0	56

od. These materials are solid DGEBA resins cured with dicy, and differ only in raw material source and date of manufacture and testing. As is seen, the data are highly reproducible. Activation energies are in good agreement with that of Sacher [3], who obtained a value of 16.6 kcal mol^{-1} for a high molecular weight liquid epoxy resin cured with dicy.

The utility of Arrhenius plots as an extrapolation technique is illustrated in Fig. 3. At high temperature where t_c is small, say less than 2 min, the determination may be subject to considerable error; indeed only with the utmost care were the data in the extreme lower left-hand corner obtainable at all. On the other hand, at low temperatures, the reaction proceeds so slowly that the rate of heat evolution becomes undetectable long before curing is complete. The experiment, even if possible on newer, more sensitive equipment, becomes very time-consuming. Cure times at 200° F ($1/K$ = 2.727×10^{-3} K^{-1}) were computed from the Arrhenius plot and are shown in Fig. 3. These systems were known to fully cure in about 2 h at 200° F, based on qualitative observations of flexibility and hardness as a function of exposure time. One can easily see that it is expedient to measure t_c at tempera-

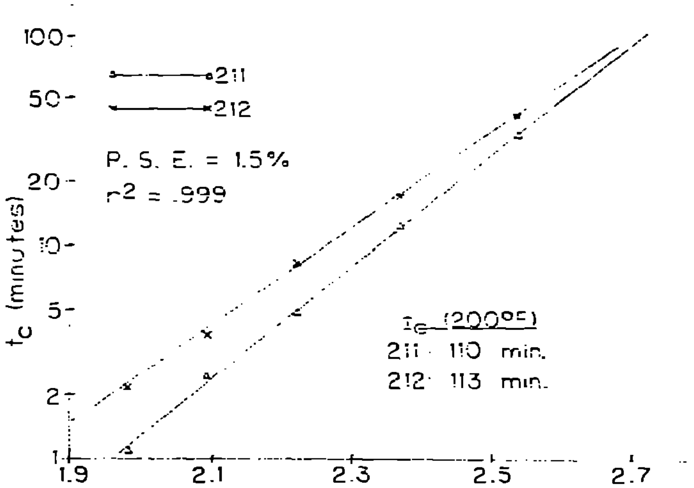

Fig. 3. Arrhenius plot for two anhydride-cured solid epoxy resins showing extrapolation to extremes of temperature.

tures such that the cure time varies from about 2 to 20 min, and extrapolate to the extreme temperature/time conditions.

As is shown by the data in Table 2, the addition of small amounts of 2-MZ (2-methylimidazole) accelerator does not significantly lower the activation energy from the unaccelerated system. This was the conclusion of Olcese et al. [12], who examined dicy-cured liquid epoxy resin systems accelerated with an imidazole derivative. This indicates that imidazoles do not catalyze the reaction of dicy with the epoxy group, but rather function as an additional co-reactant. Barton and Shepherd [15] report activation energies of 19.3—22.2 kcal mol^{-1} for the reaction of epoxy resin systems with 2-ethyl-4-methylimidazole alone. The activation energies obtained by Olcese, 14.7—19.3 kcal mol^{-1}, are slightly higher than those presented here, and can be explained by the fact that higher levels of the imidazole were used in his formulations than in those given in Table 2.

Examination of the cure time data for these systems, shown in Table 3, indicates a greater dependence of the cure time on equivalent weight of the epoxy resin, and/or dicy-to-epoxy ratio than on the level of 2-methylimidazole present.

Various hydroxyl-containing accelerators have been commonly used to enhance the cure of epoxy resins with dicy. Glycerine, tri-methylolpropane, simple alcohols, and even water have found applications as accelerators, and a mechanism for hydroxyl catalysis is given in Lee and Neville [1].

Figure 4 shows the Arrhenius plot for a heavily filled hydroxyl-accelerated, dicy-cured DER-331 epoxy resin system. This formulation contains 0.5 equivalents dicy and 0.16 moles hydroxyl groups per mole of oxirane groups. The activation energy, 12.25 kcal mol^{-1}, is significantly lower than that for unaccelerated dicy cures, indicating that hydroxyl functionally does serve as a catalyst, but does not necessarily act as a hardener itself.

The effect of carboxylic acid salts of dimethylaminomethyl phenols, such as Shell D, on the cure is shown in Table 4. Small amounts, 0.04 equivalents per equivalent epoxy, catalyze the reaction quite effectively, as is shown by the low activation energy. Additional accelerator has no effect on the activation energy, as is expected, since the same reaction is proceeding via the

TABLE 2

Compositional data and activation energies for epoxy resin systems cured with dicy and 2-methylimidazole (2-MZ)

No.	WPE	Dicy (equiv. $equiv.^{-1}$ oxirine groups)	2-MZ (equiv. $equiv.^{-1}$ oxirine groups)	ΔH_a (kcal mol^{-1})
170	580	0.75	0.05	15.7
159	785	1.6	0.05	16.8
150	785	1.4	0.035	15.1
172	570	0.7	0.05	15.8
1592	765	1.6	None	16.8
1101	706	2.0	None	16.4

TABLE 3

Cure time data for epoxy resin systems cured with dicy and 2-methylimidazole

Sample	400°F	350°F	300°F
170	3.4	9.2	
159	5.2	18.0	53.5
150	6.1	17.5	
172	3.3	10.8	32.5
1592	5.6	16.0	56
1101	4.4	12.5	

same activated complex. It is not clear from this data whether the carboxylic amine salt or the phenol group acts as the accelerator; both are probably involved to some extent [1]. Equivalent weights of accelerator were calculated based on amine functionality; phenol equivalency is lower by a factor of 3. The additional accelerator in Sample 758 did result in faster cures; cure times for Sample 766 are 15—20% longer than for Sample 758.

A series of DGEBA resin blends of average WPE of 200—212 were cured with 0.63 equivalents dicy per equivalent epoxy. The reactions were catalyzed with 0.1 equivalent hydroxyl and 0.063 equivalents of various chlorinated phenylureas. Activation energies were found to be 7.0 ± 1.4 kcal mol^{-1} for all systems studied, significantly lower than for hydroxyl catalysis alone. Use of 3-(*p*-chlorophenyl) 1,1-dimethylurea (monuron) or 3-(3,4-dichlorophenyl) 1,1-dimethylurea (diuron) did not result in significantly different activation energies, although cure times with monuron are somewhat longer. One resin system accelerated with diuron but without hydroxyl gave an activation energy of 6.8 kcal mol^{-1}, although cure times were much longer than for the systems containing hydroxyl. Catalysis via a chlorinated phenylurea-based intermediate would therefore seem to be preferred

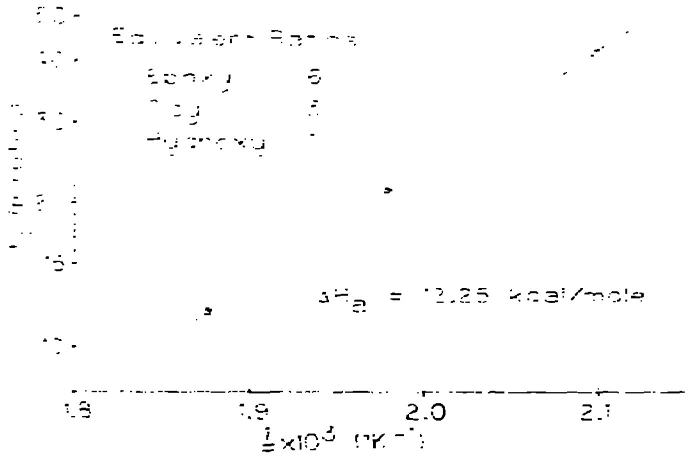

Fig. 4. Arrhenius plot for a hydroxyl-accelerated system. Equivalent ratios are: epoxy resin (DER-331), 6 equivalents; dicy, 3 equivalents; hydroxyl accelerator, 1 equivalent.

TABLE 4

Activation energies of dicy-cured DGEBA resin systems accelerated with carboxylic acid salts of dimethylaminomethyl phenols

No.	Accelerator content	ΔH_a (kcal mol^{-1})
766	0.04 equiv. equiv.$^{-1}$ epoxy	8.3
758	0.14 equiv. equiv.$^{-1}$ epoxy	8.5
Epoxy equiv. wt. = 317		
Dicy content = 0.6 equiv. equiv.$^{-1}$ epoxy		

over catalysis via the hydroxyl-based intermediate, when both catalysts are present. Typical cure times at 350° F are shown in Table 5 for comparison.

The effect of acetoguanidine as a co-curing agent with dicy was found to have only a slight effect, if any, on the activation energy. The activation energy, depicted in Fig. 5, is not significantly lower than that obtained by use of hydroxyl accelerator alone. Acetoguanidine, chemically similar to dicy itself, would not be expected to exhibit catalytic behavior.

A series of five solid DGEBA resin systems cured with trimellitic anhydride (TMA) gave an average activation energy of 12.3 kcal mol^{-1}. The epoxy resins used in this series had equivalent weights of 725—925, and were cured with 1.25—1.35 equivalents TMA per equivalent epoxy; data are summarized in Table 6.

The literature gives similar values for activation energies of anhydride-cured epoxy resin systems; these are summarized in Table 7. Except for the single high value of 18.1 kcal mol^{-1} obtained by Musatti and Macosko [19], activation energies largely fall in the range 12—15 kcal mol^{-1}, regardless of the particular anhydride or epoxy used. Macosko and Musatti were, however, in another work [7] able to obtain activation energies for hexahydrophthalic anhydride cure more in agreement with the literature. It appears that activation energies of 12—15 kcal mol^{-1} are characteristic of anhydride cures of DGEBA epoxy resins, and perhaps of all aromatic glycidyl ethers, regardless of the anhydride used. It is also apparent that carboxylic acid groups present in trimellitic and the fatty acid anhydride do not catalyze the oxirane—anhydride reaction.

This uniformity of activation energies is also apparent in cures of epoxy resins by amine curing agents. Table 8 summarizes literature values for amine

TABLE 5

Comparison of cure times of dicy-cured systems accelerated with a chlorophenylurea and chlorophenylureas plus hydroxyl

Accelerators	t_c at 350°F (min)
Diuron	33
Diuron + hydroxyl	7
Monuron + hydroxyl	9

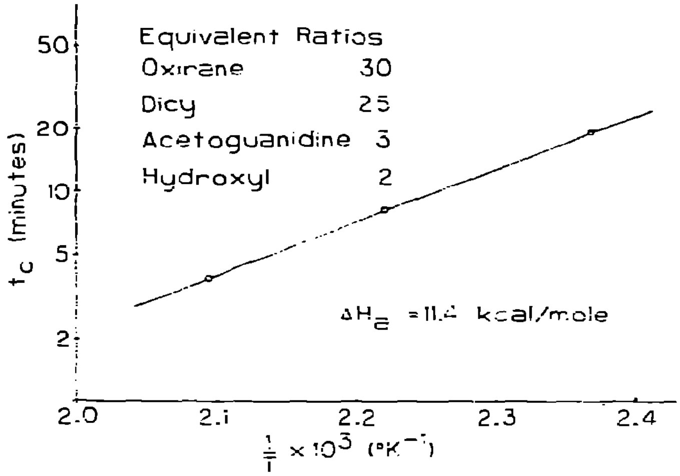

Fig. 5. Arrhenius plot for a hydroxyl-accelerated system. Equivalent ratios are: epoxy resin, 30 equivalents; hydroxyl accelerator, 2 equivalents. The liquid epoxy resin used had an equivalent weight of 174.

TABLE 6

Compositional data and activation energies of trimellitic anhydride (TMA)-cured DGEBA systems

Sample	WPE	TMA (equiv. TMA mol^{-1} oxirane)	ΔH_a (kcal mol^{-1})
211	772	1.35	10.42
212	923	1.25	12.01
214	735	1.29	12.52
215	735	1.29	12.52
216	727	1.26	13.88
		Aver. ΔH_a = 12.3	

TABLE 7

Summary of activation energies of anhydride-cured DGEBA resin systems

Anhydride	ΔH_a (kcal mol^{-1})	Ref.
Trimellitic	12.3	This work
4-Methyl-tetrahydrophthalic	12.0	4
3-Methyl-tetrahydrophthalic	14.8	4
i-Methyl-tetrahydrophthalic	13.2	4
Maleic	15.4	4
Hexahydrophthalic	12.2	6
Hexahydrophthalic	14.3	7
Fatty acid	13.4	11
Nadic methyl	11.6	16
Phthalic	14.2	17
Hexahydrophthalic	12.7	18
Hexahydrophthalic	18.1	19

TABLE 8

Summary of activation energies of amine-cured DGEBA resin systems

Amine	ΔH_a (kcal mol^{-1})	Ref.
m-Phenylene diamine	11.1—12.0	2,10,21
4,4′-Methylene dianiline	11.9—12.0	3,20
Primary aliphatic	11.8—13.9	1,18,22
Secondary aliphatic	13.4	22
N,N-Dimethyloctylamine	26.0	18
Triethanolamine	14.7	1
BF_3—hexylamine complex	13.6	18
Solid polyamine	12.7	This work

cures of DGEBA resins. From the literature data, one can see that activation energies for reactions utilizing aromatic amines fall in the range 11—12 kcal mol^{-1}, while primary and secondary aliphatic amine cures have activation energies of around 12—14 kcal mol^{-1}. A boron trifluoride—hexylamine complex gave an activation energy in the range of those for aliphatic amines also. The higher activation energies listed for reaction with the tertiary amines *N,N*-dimethyloctylamine and triethanolamine are easily explained by the fact that a different reaction is involved; cure through the hydroxyl group in the case of triethanolamine, and via formation of a quaternary amine hydroxide in the case of *N,N*-dimethyloctylamine [1]. A DGEBA resin of equivalent ratio of 1.8 equivalents amine per equivalent epoxy, gave an activation energy of 12.7 kcal mol^{-1}, well within the range of values reported in the literature.

Prime [2] has reported an activation energy of 13.3 kcal mol^{-1} for cure with a polyamide, Versamid 140 (General Mills). This polyamide contains considerable free amine groups, as does a solid polyamide examined in this study. Cure of a solid DGEBA resin with HT-2833 (Ciba) was found to proceed with an activation energy of 10.9 kcal mol^{-1} at an amine-to-epoxy ratio of 0.18. The HT-2833 does contain other functional groups capable of reacting, however, and may contain a catalyst as well. On the other hand, Prime's value of 13.3 kcal mol^{-1} for Versamid 140 cure does agree quite well with those obtained from aliphatic amine cures.

CONCLUSIONS

Isothermal DSC was seen to offer several advantages over ASTM D-1144 as a means of determining cure times. The technique is rapid, requiring only a little longer than the time needed for cure. Furthermore, the cure time at a given temperature may be obtained from a single experiment. No massive substrates or special sample preparation are needed. It is a direct method, and is independent of the variation of physical properties with degree of cure. Only a small amount of sample is needed, typically about 25 mg per

TABLE 9

Summary of activation energies for cure of DGEBA resins with various classes of curing agents

Curing agent	ΔH_a (kcal mol^{-1})
Primary and secondary amines	11—14
Aromatic	11—12
Aliphatic	12—14
Tertiary amines	26
Anhydrides	12—15
Dicy	15—17
Imidazoles [15]	19—22
Alcohols	14—15

measurement. The low thermal mass of the sample, sample container, and instrument itself allows rapid thermal equilibration, and DSC equipment has typically better temperature control than, for example, a laboratory oven.

As a means of determining activation energies, this method was found to give results comparable to those of other workers. The isothermal DSC methods are much more time-consuming than dynamic methods, but may give less ambiguous results.

We have shown here that the activation energy of the uncatalyzed reaction of DGEBA epoxy resins with various curing agents depends only on the functionality of the curing agent used, as shown in Table 9, and not on the specific curing agent involved. This was found to hold true for both lower molecular weight liquid resins and the high molecular weight solid resins. Preliminary indications are that this generalization is valid for all aromatic glycidyl ethers (such as phenyl glycidyl ether, Novalac epoxy resins), but sufficient work has not yet been done to substantiate this conclusion.

Accelerators used in dicy-cured systems can be divided into two types. Co-curing agents, such as acetoguanidine and the imidazoles, can shorten cure times, but do not affect the activation energy. Catalysts which promote ring opening, such as alcohols, the chlorophenyl ureas, and the Shell D type catalysts, substantially lower the activation energy in addition to accelerating the cure; a summary is given in Table 10. Reactions of the oxirane ring with dicy via the catalyst-based intermediate occurs in preference to the uncata-

TABLE 10

Summary of activation energies for cure of DGEBA resins with dicy and various catalysts

Catalyst	ΔH_a (kcal mol^{-1})
None	15—17
Hydroxyl	11—12
Chlorophenyl ureas	7
Shell D type	8— 9

lyzed reaction of the oxirane ring with either dicy or the catalyst alone, based on a comparison of activation energies for these three reactions.

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