

Solution Polymerizations of Epoxytetrahydrophthalic Anhydride and Its Utilization in Various Epoxy Systems

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Synopsis

Solution polymerization of epoxytetrahydrophthalic anhydride (ETHPA) has been thoroughly studied by using numerous solvents and catalysts. Products have been obtained in high yields, particularly when triethanolamine was the catalyst. This suggests that this catalyst should be considered for further applications utilizing ETHPA. However, the solution polymerization method cannot be used alone to define the effects of various catalysts on standard nonsolvated resin systems, because polymerization is greatly affected not only by the addition of solvent but also by the type of solvent. In addition, the action of the catalyst seems to depend greatly upon what solvent is employed. The reason for this dependence has not been established. The effects of the addition and reaction of ETHPA with commercial epoxy resin formulations have been investigated by means of heat distortion tests and differential thermal analyses. In most cases, although a moderate improvement was found in the thermal properties of the resins, occasional excellent results were obtained. A 10°C. increase in HDT is observed with a 2 wt.-% addition of ETHPA for bisphenol A epoxy resin-bicyclic anhydride mixture. The degree of elevation of T_g and HDT with the addition of ETHPA obviously depends not only on the composition of the resin system but also on its cure temperature. A good correlation occurs between heat-distortion temperatures and glass transition temperatures. Some few anomalous data, however, are found which point to the fact that further investigation is required before HDT and T_g can be interchanged without prior evidence of a definite relationship.

INTRODUCTION

Although a significant portion of the physical and mechanical properties of a polymer are derived from the nature of the monomer and the bonds involved, these properties also exhibit complex dependence upon intermolecular interactions and macromolecular structure. In some instances, these intermolecular forces overshadow the effect of a particular property of the monomer; nevertheless, the lack of flexibility inherent in a cyclic molecule which contains both epoxide and anhydride moieties should produce a polymer both mechanically and thermally superior to commercial epoxy resins. A polymer with the above-mentioned polymeric structure should show higher, more stable values for thermal properties and glass

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transition temperature than the usual commercial epoxy resin-anhydride systems.

The preparation of epoxytetrahydrophthalic anhydride (ETHPA)^{1,2} made available a fairly rigid compound which may be suitable for a one-component encapsulating resin. There is presently some uncertainty in the literature over the isomeric composition of the epoxidized anhydride.³ Considerable difficulty was encountered, however, in the actual melt polymerization of this compound because it decomposes and sublimates at its melting point (203.0–204.5°C.) to give friable foam with considerable weight loss.^{1,4} Some preliminary studies⁴ have indicated that solution polymerization permitted a more complete reaction and a higher molecular weight product than did melt polymerization. In order to utilize the optimum properties available from ETHPA, its polymerization must be carefully studied, preferably in solution, to obtain the simplest and most useful data from a homopolymer which is not encumbered by the presence of the usual commercial resin-anhydride system.

The primary purpose of this work was to investigate the solution polymerizations of ETHPA with particular attention to solvents and catalysts. Knowledge of these polymerizations should provide some insight toward possible practical applications of ETHPA. Similarly, solution polymerizations of commercial resin-anhydride systems were studied to determine the feasibility of this method. This approach, if applicable, would enable facile inspection and evaluation of any new resin, anhydride, or catalyst.

A second object of this study was to elucidate the effect of the incorporation of ETHPA as a tetradentate in standard epoxy systems and to introduce a quantitative relationship; four different resin systems were proposed for these explications. The characteristics studied were the heat distortion temperature (HDT) and the glass transition temperature (T_g) as determined by differential thermal analysis. Various quantities of ETHPA were incorporated into the epoxy systems, and the resultant variations in the above-mentioned thermal properties were observed.

Definite, and not unexpected, correlations between the HDT and T_g have been previously observed in this laboratory.⁵ In this study, such a relationship has been found to exist in systems not previously examined.

EXPERIMENTAL

Solution Polymerizations

The solution polymerizations were undertaken by dissolving 5.0 g. (0.0298 mole) of ETHPA in 100 ml. of solvent at the reflux temperature. The specified amount of catalyst was added while the solution was stirred; heating and stirring were continued for 7 hr. The reaction mixture, with some precipitate, was then poured slowly into 500 ml. of boiling methanol to precipitate the polymer completely and to dissolve unreacted monomer

and catalyst. The powder, usually white, was isolated by suction filtration, washed with methanol, and dried in a vacuum oven at 110°C.

Solution polymerizations of commercial resins were attempted by utilizing the above method with 3.40 g. of the diglycidylether of bisphenol A (Epi-Resz-50810), 3.58 g. of the bicyclic anhydride, methyl nadic anhydride [MNA (National Aniline) or Velsicol, methyl endic anhydride], 25–100 ml. of solvent (chlorobenzene, *o*-dichlorobenzene tetrahydrofuran, ethylene glycol monobutyl ether, or *sym*-tetrachlorethane), and 0.5–1.0 g. of catalyst [(triethanolamine (TEA), or tris(dimethylaminomethyl) phenol (TAMP)].

Melt Polymerizations

Melt polymerizations (polymerizations of simple commercial resins in the "molten" liquid state), with and without ETHPA, were run with compositions of epoxy resins 50810 (the diglycidyl ether of bisphenol A) and DEBE (the diglycidyl ether of bisphenol ether, DER-331) and anhydrides MNA and hexahydrophthalic anhydride (HHPA). These resins and anhydrides were mixed in proportion by weight to maintain a 1:1 ratio of anhydride to epoxy functional groups. The equivalent weights with respect to reactive functional moieties were considered to be: 84, 170, 157, 177, and 154 for ETHPA, 50810, DEBE, MNA, and HHPA, respectively. The resin, anhydride, and ETHPA were combined and heated to the proper temperature with stirring to dissolve the ETHPA. To this solution the catalyst was added. The mixture was cured in a polyethylene beaker in an oven to give a solid amber plug as final product.

Infrared Spectral Analyses

Infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrophotometer from mineral oil mulls of solid polymer and monomer samples. The commercial resins were used in their pure state as syrups. Solid plugs were filed to obtain the powders used in mulls for infrared spectral analyses.

Incorporation of ETHPA

Materials

The ETHPA prepared in this laboratory melted over a range of 200–203°C. and was synthesized by the reaction of peracetic acid with tetrahydrophthalic anhydride in acetic acid.^{1,6} Purification was carried out by recrystallization from *p*-dioxane, and identity was confirmed by infrared spectral analysis, elemental analysis, and by a mixed melting point with an authentic sample.

The diglycidyl ether of bisphenol A, containing some derived material of higher molecular weight, was of commercial manufacture (Hysol 2039). A single lot of this resin was used throughout this study to preclude the possibility that variations in the quantities of these species of higher

molecular weight, which can have a definite effect on properties,⁷ might prejudice the results. Likewise, and for similar reasons, single batches were used of methyl-*endo-cis*-bicyclo-(2, 2, 1)-5-heptene-2, 3-dicarboxylic anhydride (MNA), hexahydrophthalic anhydride (HHPA), diglycidyl ether of ethylene glycol CIBA resin (RD-2), and 2, 4, 6-tris (dimethylamino-methyl)phenol (DMP-30, Rohm and Haas).

Sample Preparations

In each of the following cases, the ETHPA was dissolved in the appropriate quantity of base material at the proper temperature with magnetic stirring. After dissolution of all solids, the designated catalyst or curing agent was added and the resulting mixture was sufficiently stirred and then poured to a depth of $\frac{3}{4}$ in. in a $9 \times 4\frac{1}{2} \times 1$ in. steel mold which had been properly treated with mold-release agent. The samples were then cured in a forced-draft oven within ± 2 degrees of the specified temperature.

System A. Samples containing 0, 2, 4, and 6 wt.-% ETHPA were prepared according to Table I. The resin, the bisphenol A type, and the epoxy anhydride were mixed at 100°C. After addition of curing agent, DEA (diethanolamine), the solution was poured into a cold mold and cured at 71°C. for 15 hr. and at 79.5°C. for 4 hr. to give light yellow to amber products (color darkens as ETHPA content increases).

Attempts to produce samples of System A materials containing more than 6% ETHPA failed because of the excessive precipitation of the epoxyanhydride. An attempt to overcome this difficulty by heating the material to still higher temperatures failed when gelation occurred before the sample slab could be poured.

System B. Used for these samples were 178 parts of the anhydride, MNA; 101 parts of the linear resin, RD-2, to comprise 600 g.; and 3.0 g. DMP-30 as catalyst. In this instance, a 10 wt.-% concentration of ETHPA could be obtained. The exact data are given in Table II. The resin, anhydride, and ETHPA were mixed and dissolved at 95°C.; and, after addition of the catalyst, the mixture was poured into a mold, heated to 79.5°C., and cured at 79°C. for 24 hr.

The 10% sample stood at room temperature for 1 hr. before curing; therefore, this experiment did not follow exactly the prescribed schedule. As with system A, a variation of color, light yellow to brown with increasing ETHPA, was noted with these materials.

TABLE I
System A Compositions

ETHPA, %	Wt. resin, g.	Wt. DEA, g.	Wt. ETHPA, g.
0	535.7	64.3	0
2	523.7	64.3	12
4	511.7	64.3	24
6	499.7	64.3	36

TABLE II
System B Compositions

ETHPA, %	Wt. resin, g.	Wt. MNA, g.	Wt. ETHPA, g.
0	217.5	382.5	0
2	213.2	374.8	12
4	208.9	367.1	24
6	204.6	359.4	36
8	200.3	351.7	48
10	196.0	344.0	60

System C. Once again, 100 parts of the bisphenol A resin were used with 80 parts of hexahydrophthalic anhydride (HHPA) (600 g. total), and 3.0 g. of DMP-30 catalyst. The materials were mixed at 90°C., poured into a preheated mold, allowed to stand at room temperature for 15 min., and then cured at 71°C. for 24 hr. and at 134°C. for 8 hr. Specific information is given in Table III. All slabs obtained were brown in color.

TABLE III
System C Compositions

ETHPA, %	Wt. resin, g.	Wt. HHPA, g.	Wt. ETHPA, g.
0	333.0	267.0	0
2	326.3	261.7	12
4	319.6	256.4	24
6	312.9	251.1	36
8	306.2	245.8	48

Several attempts were made to produce samples with ETHPA concentrations in excess of 8%. All these failed, either because excessive precipitation occurred, or because the reaction took place with such vigor that the sample was cracked and bubbled.

System D. The base material for this mixture was 100 parts of the bisphenol A resin and 90 parts of the anhydride MNA (600 g. total), with 2.8 g. of DMP-30 as a catalyst. Components were mixed at 98°C., poured into a preheated mold, then allowed to stand at ambient conditions for 2 hr. before being cured at 93°C. for 24 hr., at 149°C. for 3³/₄ hr., and finally at 204°C. for 4 hr. Data are given in Table IV.

TABLE IV
System D Compositions

ETHPA, %	Wt. resin, g.	Wt. MNA, g.	Wt. ETHPA, g.
0	315.5	284.5	0
2	309.2	278.8	12
4	302.9	273.1	24
6	296.6	267.4	36
8	290.3	261.7	48
10	284.0	256.0	60

As ETHPA content increased, the gelation at room temperature became more rapid, and the color of the final product progressed from a light yellow (0%) to a dark brown (10%).

Postcuring

The additional postcures given to systems A, B, and C are summarized in Table V.

TABLE V
Postcuring Data

System	Temp., °C.	Time, hr.	Observations
A, C	149	3.5	A: Severe darkening to opaque black; C: darkening
	204	18	
B	107	7	Darkening
	121	16	
	149	24	
	204	18	

These postcures were conducted on heat-distortion test bars. After these bars were heated to the maximum temperature indicated, they were allowed to cool slowly (anneal) to room temperature.

Thermal Analyses

From the slabs of cured epoxy resin, bars for heat-distortion tests were fabricated ($1/2 \times 1/2 \times 5$ in.) as per the ASTM test D-648. Five bars were taken from each sample; values for HDT in this report are average sample values.

Following the heat-distortion tests, a procedure developed in this laboratory was used to determine T_g .⁸ Small cylinders ($1/16$ in. diameter) were prepared by using a hollow, flanged drill bit. These cores were again drilled to accept a thermocouple and used to determine the glass transition temperature (T_g) on a Du Pont 900 differential thermal analyzer (DTA). From the curves so obtained the first inflection point was assigned as the glass transition temperature.

RESULTS AND DISCUSSION

Solution Polymerization of ETHPA

Table VI shows the numerous combinations of solvents and catalysts which were attempted for the solution polymerization of ETHPA. The solvents included dioxane, *o*-dichlorobenzene, chlorobenzene, trichloroethylene, dimethylformamide (DMF), toluene, dimethyl sulfoxide (DMSO), 1,2-dichloroethane, 1,1,2-trichloroethane, and *sym*-tetrachloroethane. Although most solvents were acceptable, some solvents caused low-yield precipitation of a low molecular weight polymer, or decomposition of the monomer and polymer with prolonged heating. Table VI and Figures

1-3 show that the most satisfactory solvents are chlorobenzene, *o*-dichlorobenzene, and *sym*-tetrachloroethane.

The most satisfactory catalysts for the solution polymerization of ETHPA were triethylenediamine (TEDA) and triethanolamine (TEA). Those catalysts studied were bases consisting of primary, secondary, and tertiary amines, including benzyldimethylamine (BDMA), triethylene-

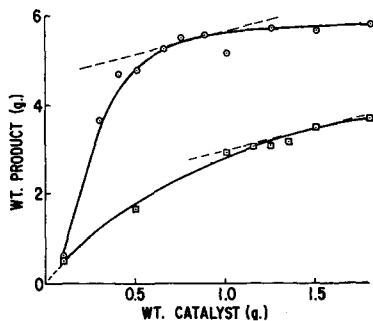


Fig. 1. Polymerization of epoxytetrahydrophthalic anhydride with TEDA (triethylenediamine) (○) in *o*-dichlorobenzene and (◻) in chlorobenzene.

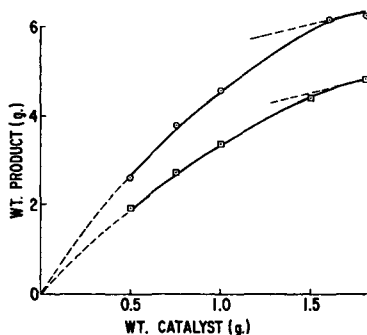


Fig. 2. Polymerization of epoxytetrahydrophthalic anhydride with triethanolamine (○) in *o*-dichlorobenzene and (◻) in chlorobenzene.

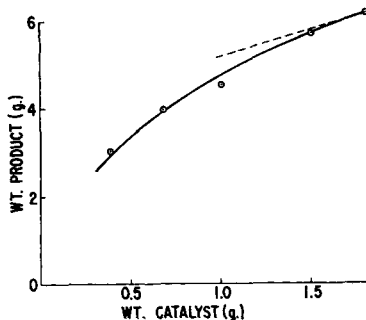


Fig. 3. Polymerization of ETHPA with triethanolamine in *sym*-tetrachloroethane.

TABLE VI
 Data for Solution Polymerizations

No.	Catalyst and amount, g.	Solvent (100 ml.)	Yield, g. ^a
1	BDMA, 0.084	Dioxane	NR ^b
2	TEDA, —	<i>o</i> -Dichlorobenzene	See Fig. 1
3	TEDA, —	Chlorobenzene	See Fig. 1
4	TEDA, 1.0	Trichloroethylene	3.93 ^c
5	TEDA, 1.0	DMF	3.62
6	TEDA, 1.0	Toluene	1.55 ^c
7	TEDA, 1.0	DMSO	NR ^d
8	TAMP, 0.782	<i>o</i> -Dichlorobenzene	3.96 ^d
9	BDMA, 1.0	<i>o</i> -Dichlorobenzene	1.39
10	TEDA, 0.75	1,2-Dichloroethane	3.83 ^d
11	TAMP, 1.0	Chlorobenzene	0.12
12	BDMA, 1.0	Chlorobenzene	0.91
13	TEA, —	Chlorobenzene	See Fig. 2
14	TEA, —	<i>o</i> -Dichlorobenzene	See Fig. 2
15	TEA + ArOH, 0.75 + 0.47	Chlorobenzene	2.98
16	TEA + ArCO ₂ H, 0.75 + 0.61	Chlorobenzene	2.85
17	TEA + BuOH, 0.75 + 0.37	Chlorobenzene	2.64
18	ArOH, 0.94	Chlorobenzene	NR
19	ArCO ₂ H, 1.22	Chlorobenzene	NR
20	Pyridine, 0.4	Chlorobenzene	Trace
21	TEDA, 1.0	<i>sym</i> -Tetrachloroethane	NR
22	TEDA, 1.0	1,1,2-Trichloroethane	5.23 ^d
23	TEA	<i>sym</i> -Tetrachloroethane	See Fig. 3
24	TEA, 1.0	1,1,2-Trichloroethane	4.26 ^d
25	<i>M</i> -Toluidine, 1.0	<i>sym</i> -Tetrachloroethane	Gum
26	<i>M</i> -Toluidine, 1.0	1,1,2-Trichloroethane	Gum
27	<i>M</i> -Toluidine, 1.0	Chlorobenzene	Gum
28	<i>M</i> -Toluidine, 1.0	<i>o</i> -Dichlorobenzene	Gum

^a From 5.0 g. of ETHPA (see Experimental Section).

^b No reaction.

^c The infrared spectrum showed incomplete polymerization.

^d Decomposition and/or discoloration of the monomer or polymer occurred.

diamine (TEDA), tris(dimethylaminomethyl)phenol (TAMP), triethanolamine (TEA), *m*-toluidine, and pyridine. Organic acids, including phenol and benzoic acid, were also investigated. Contrary to other epoxy resins,^{9,10} ETHPA was not polymerized by organic acids or alcohols either as sole catalysts or as co-catalysts with tertiary amines.

Figures 1–3 are graphs of yield versus amount of catalyst for the best combinations of catalyst and solvent. In all graphs it is seen that the curves approach asymptotically a line which represents simple linear addition of catalyst. At the point of convergence, additional catalyst merely adds the weight of the catalyst to the yield, but no further conversion of monomer occurs, even though some monomer is unaccounted for. Beyond this point, further addition of catalyst serves only to decrease the average molecular weight, because more polymer chains are initiated. Some yield versus catalyst curves (Fig. 1, with dichlorobenzene) even tend

to fall away from this asymptote. This indicates that, beyond an optimum amount, the catalyst is not being utilized at all, even in the production of lower molecular weight fractions. This utilization and incorporation of excess catalyst appears to be a function of solvent type.

From Figures 1 and 2 it is obvious that, regardless of the catalyst, *o*-dichlorobenzene is a better solvent than chlorobenzene. This is probably a matter of solvating ability and boiling point (reaction temperature of polymerization). Figure 3, compared to Figure 2, demonstrates the similarity between *o*-dichlorobenzene and *sym*-tetrachloroethane as solvents with TEA as the catalyst. The above figures also show that TEA is a slightly better catalyst than TEDA. Note that, although TEDA is acceptable in *o*-dichlorobenzene, it affects no reaction in *sym*-tetrachloroethane. Likewise, *sym*-tetrachloroethane is suitable in most cases as a solvent, but 1,1,2-trichloroethane usually facilitates decomposition and discoloration of the product.

There is evidently no correlation of product yield and quality to solvent dielectric constant and boiling point. Similarly, the effect of catalysts varies considerably from solvent to solvent. These effects appear to result from extremely complicated catalyst-solvent interactions which introduce variables that have not been analyzed in this study. Also, it is unfortunate, due to product insolubility, that the only applicable criteria by which these insoluble crosslinked powders of polymerized ETHPA can be judged are visual inspection, infrared spectrometry, and yield.

The above data should be sufficient to recommend use of triethanolamine when polymerizing ETHPA with mixtures of commercial epoxy resins. The data also show that some catalysts such as TAMP, which are suitable for commercial resins, are unsatisfactory for the polymerization of ETHPA.

Infrared spectra were used to test for completeness of polymerization in all products because these spectra indicated the disappearance of epoxy and anhydride bands. On the spectrum for ETHPA appear the epoxide band at 793 cm.^{-1} and two anhydride bands at 1840 and 1770 cm.^{-1} . The spectra of polymerized ETHPA samples are greatly simplified, the epoxy band has disappeared, and the anhydride bands have shifted to lower ester frequencies (1730 – 1790 cm.^{-1}) and have nearly coalesced.

The polymerizations of commercial resin-anhydride mixtures in solution gave very discouraging results, because either the yields for all products were very low or they were low molecular weight, partially decomposed gummy substances. This again indicates that solvent properties and boiling point exert an overpowering and complex effect on this polymerization reaction. Indeed, these results point out the futility of using solution polymerization as a check on most polymerizations of commercial resins.

Incorporation of ETHPA into Resin Systems

Four epoxy resin and resin-anhydride systems were utilized in this part of the study: (A) the diglycidyl ether of bisphenol A cured with diethanolamine; (B) the diglycidyl ether of ethylene glycol cured with methyl-endo-

cis-bicyclo-(2,2,1)-5 heptene-2,3-dicarboxylic acid anhydride (MNA); (C) the diglycidyl ether of bisphenol A cured with hexahydrophthalic anhydride (HHPA); and (D) the diglycidyl ether of bisphenol A cured with MNA.

These materials were chosen to permit investigation of the effects of incorporation of ETHPA into (1) a standard amine-cured system, (2) standard anhydride-cured systems, and (3) an anhydride-cured aliphatic system (system B).

Table VII presents the HDT and T_g data for system A. The values are given for the cured system and for the system after postcure. The limits of solubility for ETHPA in this material seemed to have been reached at a point at which the ETHPA constituted 6% of the weight of the cured material. The addition of the ETHPA seems to have had little or no effect, beyond experimental error, on the HDT or the T_g . It was thought that the comparatively low temperature of the initial cure might have resulted in little or no effective incorporation of the ETHPA into the polymer, especially since the temperature required to initiate reaction in the pure crystalline ETHPA is approximately 205°C. To check this possibility, the samples from system A were postcured, which resulted in considerable darkening of the material. Instead of raising the HDT and T_g values, the postcuring produced a lowering of these in all cases except for the sample containing 6% ETHPA. This anomalous behavior may be attributed to the fact that considerable decomposition of the material took place during postcure. The effect of this degradation seems to have been offset to some extent in the samples containing 4 and 6% ETHPA, presumably by further reaction of the epoxy anhydride. It is noteworthy that the T_g values of the postcured samples show the same regular progression, but at a lower value than the HDT. This relationship has been noticed before in this laboratory^{5,11} and is not unexpected, as it seems to occur for most resins. A further discussion of this relationship will ensue later in this report.

TABLE VII
System A: Bisphenol A Resin with Diethanolamine

ETHPA, %	Cured		Postcured	
	HDT, °C.	T_g , °C.	HDT, °C.	T_g , °C.
0	94	89	87	85
2	94	90	94	87
4	96	93.5	97	90
6	96	89	99	92

Data for system B are presented similarly in Table VIII. The greater solubility of ETHPA in the base material allowed production of samples in which the epoxy anhydride constituted up to 10% of the final weight of the cured material. Since the resin is linear, and there was a noticeable hardening with the addition of increasing percentages of ETHPA, it was expected that a significant increase in HDT and T_g would likewise be noted. After

TABLE VIII
System B: Linear Glycol Resin with MNA

ETHPA, %	Cured		Postcured	
	HDT, °C.	T_g , °C.	HDT, °C.	T_g , °C.
0	62	55	64	56
2	65	62	71	66
4	65	58	74	70
6	66	52	75	66
8	68	66	82	75
10	60	48	86	79

the initial cure, the improvement was unexpectedly small in all cases; furthermore, a detrimental effect was found in the case of the 10% sample, which was an opaque black. Once again this was presumed to result from decomposition as carbonization, perhaps in turn deriving from a high-reaction exotherm. Since the samples after postcuring exhibited a reasonable improvement in HDT, the results after initial cure may be explained in terms of inadequate incorporation of the epoxy anhydride. The T_g , being somewhat low, demonstrated repeatedly its correlation to HDT, except for anomalous 6% sample for both simple cure and postcure.

Systems C and D were composed of diglycidyl ether of bisphenol A cured with HHPA and MNA, respectively. These systems exhibited truly promising improvement. This was somewhat surprising, since the HDT and T_g of the unmodified base materials for these systems are relatively high, and the advantage of tetradentate addition would be expected to be somewhat obscured. Figure 4 is a plot of HDT and T_g versus per cent ETHPA by weight in the cured sample for system C. Here the increase in HDT and T_g with increasing ETHPA concentration is clearly apparent. This effect, contributed by the epoxyanhydride, may be attributed to the higher cross-link density, which in turn seems to be manifested in the higher thermal properties of this system. Fortunately, this particular experiment seems to be virtually devoid of complicating factors. A higher initial cure might have increased the observed effect, however, and this is indicated in Figure 5, which is a plot of HDT and T_g values for system C after the samples were postcured. These data again support the hypothesis that cure temperature

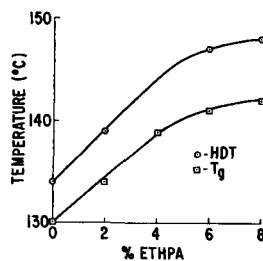


Fig. 4. System C simple cure, bisphenol A-type resin with hexahydrophthalic anhydride.

strongly influence^{1,9} the degree of effective incorporation of ETHPA into the polymer system. They further suggest that decomposition accompanying a high reaction temperature was responsible for the failure of system A to exhibit similar behavior. It should be noted that the data for the cured and postcured control samples (0% ETHPA) show little effect of postcure (HDT's of 134 and 136°C., respectively). However, as ETHPA content increases, the effect of postcure likewise increases, presumably due to the more effective incorporation of the rigid, crosslinking agent, ETHPA.

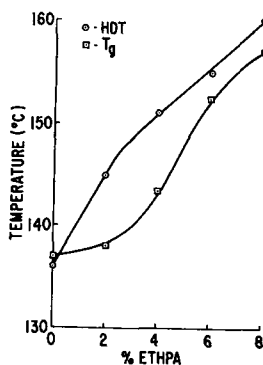


Fig. 5. System C postcure, *bis*phenol A type resin with hexahydrophthalic anhydride.

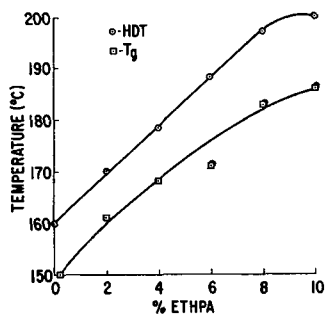


Fig. 6. System D: *bis*phenol A-type resin with methyl nadic anhydride.

From Figures 4 and 5, the correlation between the heat distortion and glass transition temperatures would seem to be amply demonstrated. After consideration of all the factors involved and experimental error, the T_g was found in all instances to follow the HDT at somewhat lower values. This relationship is plausible when one examines these tests and what they actually measure. The HDT is an ASTM test (D-648) which determines a temperature at which a standard deflection takes place under controlled conditions. Theoretically, before this deformation can take place, the material must be heated to the secondary transition temperature (the T_g), where secondary bond forces between chain segments begin to weaken and

disintegrate, and to allow the specimen to become soft and flexible. Only after this temperature has been passed in the heating cycle can the bar be deformed sufficiently to give a reading for heat distortion.

Although DTA is a useful and proven tool, recent investigations¹² in these laboratories have indicated that the second inflection point on the DTA curve is a more reliable or reproducible indication of the T_g for these materials. Further, for these resin systems, both values should perhaps be noted as a range as with melting point data. This procedure would result in even a closer correlation between HDT and T_g .

Finally, Figure 6 presents the data for the most successful system studied (D), a mixture of the standard epoxy resin with a substituted bicyclic anhydride. A nearly 10°C. rise in HDT is observed for every 2 wt.-% increment in ETHPA content. It is considered that the high cure temperature used is responsible in part for this unusually high response to the addition of an epoxy anhydride. As a saturation point is reached in both systems C and D in relation to the solubility of ETHPA (10%), a leveling off of this pronounced effect is evident. The decrease is conceivable in that, at the saturation point, optimum reaction and effect are no longer obtainable. It is proposed then that, even if more ETHPA could be dissolved in the monomeric solution, no further increase, and perhaps even a decrease, in thermal properties may be observed.

The infrared spectral studies of these commercial resin-anhydride-ETHPA products have shown that the ETHPA has completely reacted. When the spectra of the component parts are compared with the spectrum of ETHPA, it is readily noted that the epoxide bands from ETHPA (793 cm.^{-1}) are not present in the spectrum of the cured mixture. Also, the anhydride bands from ETHPA at 1840 and 1770 cm.^{-1} become but a single ester band at 1730 cm.^{-1} . However, the presence of a weak epoxide band arising from the glycidyl ethers indicates incomplete reaction of this component. The spectrum of cured resin is greatly simplified compared to the spectra of its components. The spectrum of the cured resin has broad weak bands; whereas, the spectra of the resin components have sharply defined bands. This behavior in the infrared region is to be expected in a complex thermoset resin.

One anomalous and peculiar observance is the correlation between T_g and HDT for system D. Although the HDT rises linearly to the saturation point, the T_g falls away more rapidly than expected, and is somewhat irregular. This behavior is difficult to explain and perhaps can best be used to demonstrate the need for caution when indiscriminately replacing heat-distortion data by glass transition temperatures from differential thermal analysis.

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