

Cure of Epoxy Resins with Aromatic Amines: High Heat-Distortion Studies*

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Synopsis

Castings having unexpectedly high heat-distortion temperatures result when certain treated resins of the EPON† 828 type and about 75% of the stoichiometric amount of *m*-phenylenediamine, are postcured for 10–20 hr. at 175–200°C. The improvement in heat-distortion temperature is about 100°C., to values as high as 250°C. A recrystallized resin has given the highest values. Other glycidyl ethers of polyphenols have shown this phenomenon to a lesser degree, but other amine curing agents, including isomers and substitution products of *m*-phenylenediamine, have not. Some evidence of a new curing reaction has been developed, by NMR and pyrolysis studies of model compounds, which supports the postulate that the *m*-phenylenediamine is alkylated with a fifth epoxy group during the postcure, presumably at a ring carbon, resulting in greater crosslinking.

INTRODUCTION

A widely used epoxy resin system having good solvent resistance, good mechanical properties, and good high-temperature properties is that involving EPON 828 (Shell Chemical Co.), a liquid resin nominally the diglycidyl ether of bisphenol A (BPA), cured with the aromatic amine, *m*-phenylenediamine (CL).‡¹ A typical formulation involves the use of 14 parts of CL per hundred parts of resin, and a cure schedule of 2 hr. at 80–100°C. plus 2 hr. at 150°C. The heat-distortion temperature (HDT) of such a resin is about 150°C. It has been reported² that the HDT of this system can be raised by the use of a special resin, a reduced amount of curing agent, and a more severe cure. In our studies of this unusual curing reaction, it has been found that the HDT can be increased by 100°C., to values above 250°C. The present work describes some of the most effective resin-curing agent combinations and gives evidence of a new curing reaction.

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† EPON is a registered trademark of the Shell Oil Company.

‡ The source of this curing agent was E. I. DuPont de Nemours, Dyes and Chemicals Div. For simplicity, the abbreviation "CL" has been used in this paper.

RESIN SELECTION AND STOICHIOMETRY

Resins Based on Bisphenol A

Castings $\frac{1}{2}$ in. square and 5 in. long were made from Epon 828 and resins treated by crystallization from solvents or by molecular distillation, at CL/epoxide ratios varying from 60 to 100% of stoichiometric. Samples were cured for 2 hr. at 100°C., 2 hr. at 150°C., and 14–20 hr. at 200°C. Properties of the liquid bisphenol A-epichlorohydrin-based resins are given in Table I. The variations in HDT with resin used and with amine/epoxide ratio are shown in Figure 1. The HDT was determined at 264 psi fiber stress, according to ASTM D648-56. A maximum in the HDT was observed with all resins at about 75% of the stoichiometric amount of CL, the height of the maximum varying considerably with the resin used. Thus, the greatest HDT observed with Epon 828 was 181°C. and with the recrystallized grades, Epon resins X-24 and X-22, 217 and 232–254°C., respectively. Several other resins, including a distilled grade, gave intermediate values. The highest HDT values resulted from the use of resins that approach the diglycidyl ether of bisphenol A in composition. There is a rough, inverse correlation of chlorine content of the resin with maximum HDT.

A similar maximum was noted for the flexural strength of castings from EPON X-22 and CL. Figure 2 shows the flexural strength at 300°F. as a function of the amount of amine used. Thus, certain mechanical properties can be expected to follow the improvement in HDT, but for simplicity, the present discussion will be limited to HDT effects.

Higher molecular weight resins based on BPA, EPON 834, and EPON 1001, gave castings which showed some increase in HDT with decreased CL concentration, but the effect was progressively less than with EPON 828. The HDT of postcured castings made with 80 and 100% of the stoichiometric amount of CL is shown in Figure 3, as a function of the epoxy value of several BPA-based resins. It is seen that the HDT, and especially the increase in HDT with a deficiency of curing agent, increased considerably with the epoxy value of the resin. The Δ HDT varied from 2°C. with EPON 1001 to 42°C. with Epon X-22. The absolute value of the HDT of the postcured casting is related to the equivalent weight of the resin, and per-

TABLE I
Properties of EPON 828 and Treated Resins

Resin	Method of treatment	Epoxide value, eq./100 g.	Hydroxyl value, eq./100 g.	Total chlorine, wt.-%
EPON 828	—	0.528	0.05	0.24
EPON H 825	Molec. distillation	0.554	0.03	0.15
EPON X-24	Recrystallized	0.577	—	0.06
EPON X-22	Recrystallized	0.590	0.01	0.06

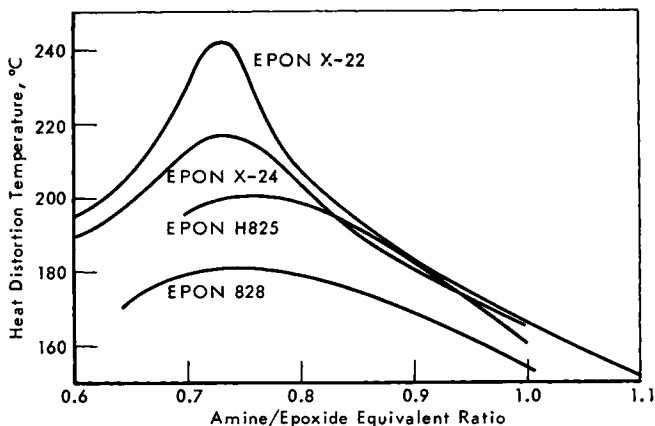


Fig. 1. Heat-distortion temperature of postcured castings from EPON 828-type resins and CL.

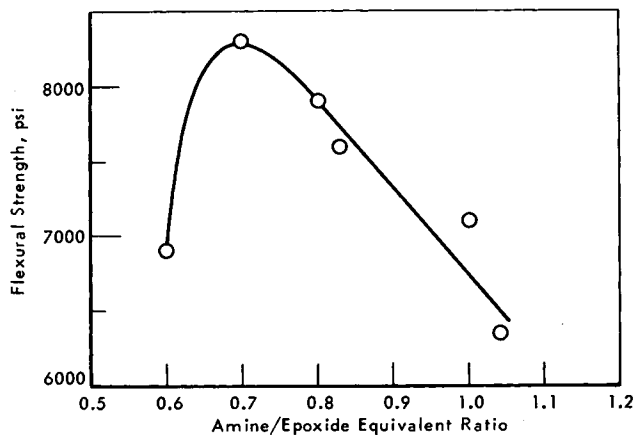


Fig. 2. Flexural strength at 149°C. of postcured castings from EPON X-22 and CL.

haps to the approach to difunctionality, but the increase in HDT may depend more on the presence of chlorine or hydroxyl, or on steric or mobility factors resulting from the presence of higher molecular weight homologs.

Other Epoxy Resins

Several other epoxy resins were tested in a similar manner, with the results shown in Figure 4. Increases in HDT with decreasing CL concentration were noted with resorcinol diglycidyl ether, the diglycidyl ether of bisphenol F, and a low-viscosity epoxidized novolac, but the general HDT level was low, below 170°C. A higher-viscosity epoxy novolac and a 1/1 mixture of EPON 1031 and EPON 828 showed increases in HDT, from 205–215°C. to greater than 260°C. at 100% and 80% CL stoichiometry, respectively.

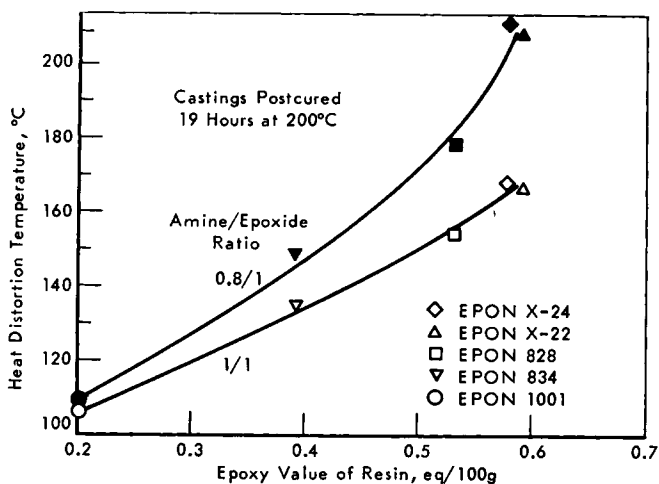


Fig. 3. Heat-distortion temperature of CL-cured castings as a function of epoxy value of BPA-type epoxide.

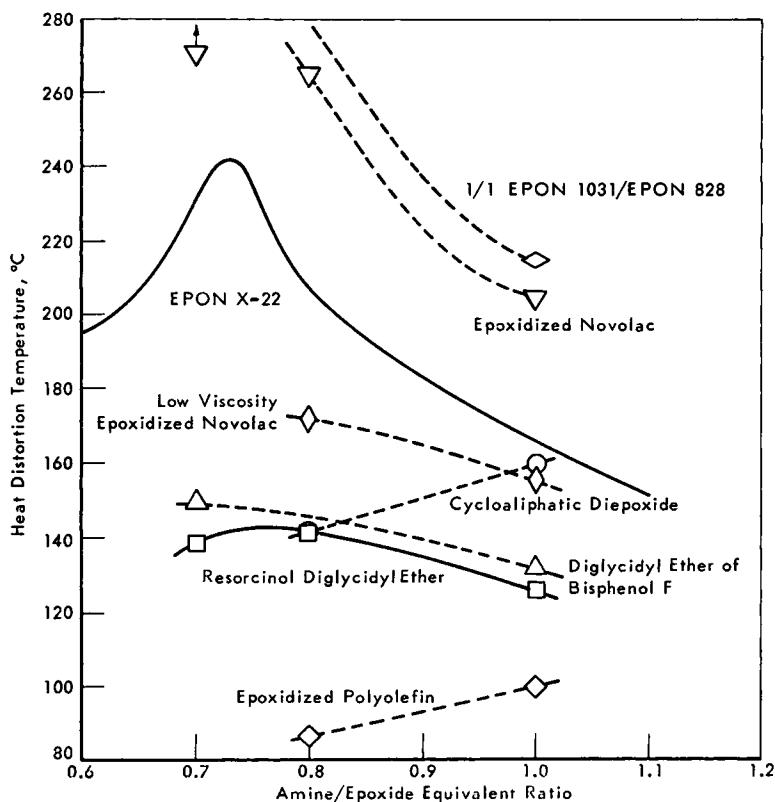


Fig. 4. Heat-distortion temperature of postcured castings from various epoxy resins and CL.

When epoxy resins other than the glycidyl ethers of polyphenols were tested, it was found that decreasing the CL concentration resulted in a drop in HDT. These resins included a cycloaliphatic type, and an epoxidized olefin type.

Effect of Postcuring Conditions

The previously reported data have all been based on castings postcured in a forced draft oven for 14–20 hours at 200°C. after an initial oven cure for 2 hr. each at 100 and 150°C. To demonstrate that such a postcure is effective, the HDT was determined in a series of castings made from EPON X-22 and varying amounts of CL, both after the initial cure, and, on the recovered samples, after a 19-hr. postcure at 200°C. From Figure 5, it can

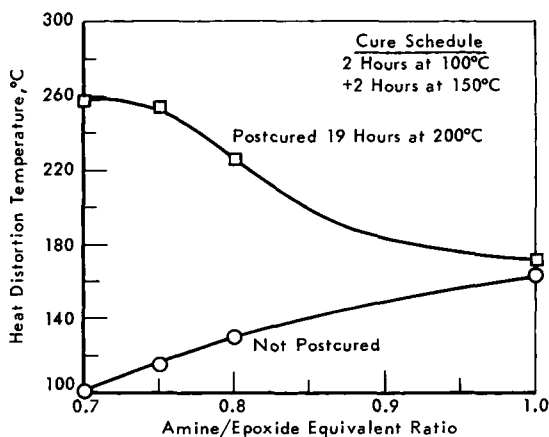


Fig. 5. Increase in heat distortion temperature of EPON X-22/CL castings after postcure.

be seen that the HDT of the initially cured samples fell off badly with the amine concentration, from about 163°C. at a 1/1 amine/epoxide ratio to only 100°C. at a 0.7/1 ratio. Subsequent postcure increased the HDT only slightly at the 1/1 ratio, but by more than 150°C. at the 0.7/1 ratio, to a value of 257°C. These results very strongly indicate that a new curing or crosslinking reaction takes place during postcure, and only when the amine is present in a deficient amount.

Temperature of Postcure

The best postcuring temperature appears to be in the range of 175–200°C. After 4 hr. at 250°C., the HDT of EPON X-22/CL castings made at 0.75/1 amine/epoxy ratio was low (only 170°C.), presumably because of thermal degradation. Postcuring for 19 hr. at 200 or 175°C. gave HDT values of about 240°C., and at 150°C., the HDT was only 179°C.

Length of Postcure

At a postcure temperature of 200°C., the maximum HDT value was approached in about 12 hr., as is shown in Figure 6. After 48 hr. the HDT had dropped to 190°C. The optimum period appears to be about 12–24 hr.

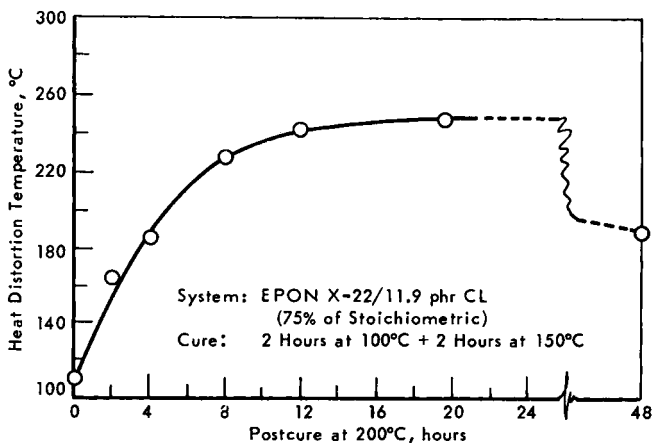


Fig. 6. Effect of length of postcure on heat-distortion temperature.

TESTING OF POLYAMINE CURING AGENTS

The work previously discussed has all involved the widely used aromatic amine curing agent, *m*-phenylenediamine (CL). It was of interest to learn whether other aromatic amine curing agents behaved in a similar manner when present in lower than the stoichiometric amount, and Figure 7 and Table II present the HDT data obtained when various amines were used to cure Epon X-22. The amines tested included *o*- and *p*-phenylenediamines; 2,4-diaminoanisole; 2,4- and 3,4-toluenediamines; 2,4-diaminodiphenylamine; 4,4'-methylenedianiline; 4,4'-diaminodiphenylsulfone; diaminodixylylsulfone; *m*-xylylenediamine; and 1,3-diaminocyclohexane. It is immediately apparent that none of the amines tested showed the large increase in HDT found for CL. To the contrary, most of the amines, when used at 80% of the stoichiometric amount, gave castings with appreciably reduced HDT's. In this connection, three lots of technical grade *m*-phenylenediamine gave similar results; two samples were from du Pont, and one from Allied Chemical. When used at the stoichiometric level, a few curing agents do, of course, give higher HDT's than does CL; these include 4,4'-diaminodiphenylsulfone and 4,4'-methylenedianiline.

It is interesting to compare the behavior of *o*- and *p*-phenylenediamines with that of the *meta* isomer. The difference in HDT between postcured castings made with 100% and 80% of the stoichiometric amine concentration was +3°C. with the *ortho* compound, -16°C. with the *para* isomer, and +41°C. with the *meta* isomer. Decreases in HDT were also observed

TABLE II
Heat-Distortion Temperature of Castings
from EPON X-22 Cured with Various Polyamines

Compound	Curing agent Source	Curing agent		Cure sched- ule, °C.	HDT, °C.
		Amt., phr	% of stoich.		
<i>m</i> -Phenylenediamine	du Pont, tech	15.9	100	a	168
		12.7	80	a	208
<i>o</i> -Phenylenediamine	Eastman, P1700	15.9	100	a	174
		12.7	80	a	177
<i>p</i> -Phenylenediamine	Eastman, P394	15.9	100	a	167
		12.7	80	a	151
2,4-Diaminoanisole	Matheson, Coleman and Bell	20.3	100	a	152
		16.2	80	a	155
2,4-Toluenediamine	Eastman, T458	18.0	100	a	163
		14.3	80	a	158
3,4-Toluenediamine	Eastman, P4273	18.0	100	a	160
		14.3	80	a	156
2,4-Diaminodiphenyl- amine	Eastman, P8011	23.5	100	a	200
		18.7	80	a	183
4,4'-Methylene- dianiline	Eastman, P756	29.1	100	b	182
		23.3	80	b	163
4,4'-Diaminodiphenyl sulfone	du Pont	33.5	91	c	228
		26.8	73	c	195
Diaminodixylyl sulfone	Chemetron	44.6	(100)	d	168
		35.6	(80)	d	146
<i>m</i> -Xylylenediamine	Oronite	20.0	100	e	120
		16.0	80	e	117
1,3-Diaminocyclo- hexane	Experimental	16.5	100	f	138
		14.5	80	f	126

^a 2 hr., 100°C., + 2 hr., 150°C. + 14–20 hr., 200°C.

^b 16 hr., 55°C. + 2 hr., 125°C. + 2.5 hr., 175°C. + 17 hr., 200°C.

^c 22 hr., 150°C. + 19 hr., 200°C.

^d 1 hr., 135°C. + 3.5 hr., 150°C. + 19 hr., 200°C.

^e 1 hr., 80°C. + 1 hr., 100°C. + 2 hr., 150°C. + 19 hr., 200°C.

^f 2 hr., 35°C. + 2 hr., 60°C. + 1 hr., 90°C. + 1 hr., 150°C. + 16 hr., 200°C.

with substituted *m*-phenylenediamines, containing either a methyl, a methoxy, or an aminophenyl group in the 4-position. 1,3-Diaminocyclohexane, hydrogenated *m*-phenylenediamine, similarly gave castings of lower HDT when used in a deficient amount. It thus appears that the large increases in HDT observed with CL are unique to that curing agent.

When one considers that CL is the only amine giving rise to castings of increased HDT, and that the HDT reaches its maximum at about 73–80% of the normal stoichiometric amount, it can be reasoned that the functionality of the CL has increased from the normal value of 4 to a value of 5–5.5. An increase in functionality would result in increased crosslinking, and greater HDT. Either the 2- or the 4-position on the CL ring should be more reactive than in the case of the *ortho* or *para* isomers. Since block-

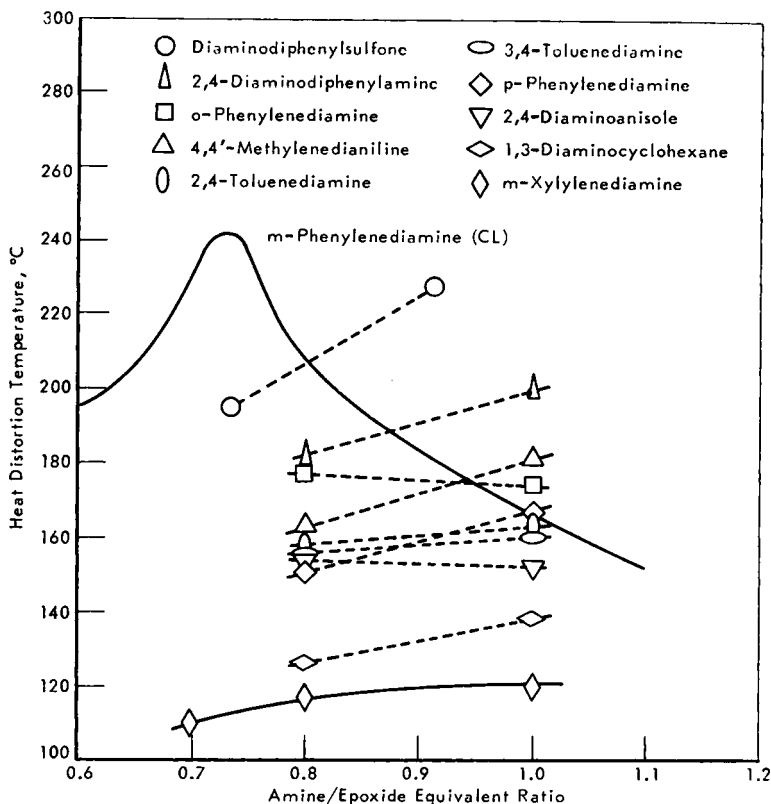


Fig. 7. Heat-distortion temperature of postcured castings from EPON X-22 cured with various atomic diamines.

ing of the 4-position apparently prevented the HDT increase, the 4-position may be the site of a new curing reaction. Reaction could also take place at the 6-position, thus accounting for functionalities greater than 5.

STUDIES OF THE CURING MECHANISM

Examination of Cured Resins

Examination of cured resin samples of low and high HDT by infrared spectroscopy or by pyrolysis at 475°C. followed by GLC analysis of the distillate by the technique of Dimbat and Eggertsen³ showed no interpretable differences between samples. The density of the castings was observed to decrease slightly during the postcure, for example, from 1.207 to 1.201 g./ml. at 25°C. in the case of CL and EPON X-22 at an equivalent ratio of 0.75/1. This suggests that no cyclic structures formed during postcure.

Near-Infrared Spectra during Cure

Following the cure by means of near-infrared spectroscopy⁴ was more helpful. With stoichiometric amounts of amine and EPON X-22, curing for 2 hr. each at 100 and 150°C. resulted in substantially complete disappearance of epoxy (band at 2.205 μ), primary amine (1.98 μ), and secondary amine (1.50 μ), with the formation of hydroxyl (1.43 μ). The spectrum was unchanged after postcure, as shown in Figure 8. With a deficiency of amine (excess of epoxide), the primary and secondary amine bands disappeared after cure, hydroxyl was formed, and some epoxide remained. Upon postcure, the epoxy disappeared, the amine groups were still absent, and additional hydroxyl was formed, the increase being estimated at about 40%. These changes are shown in the spectra in Figure 9. Minor spectral changes, of unknown significance, were noted, including the appearance

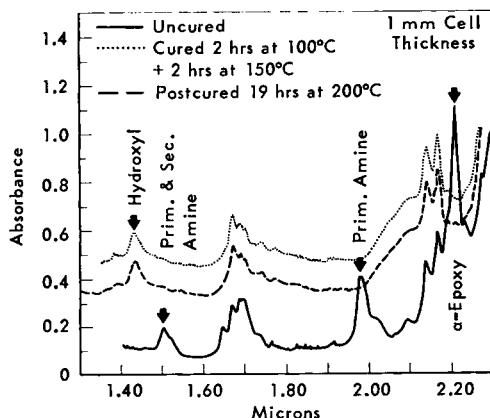


Fig. 8. Near-infrared spectra during cure of EPON X-22/CL (amine/epoxide ratio = 1/1).

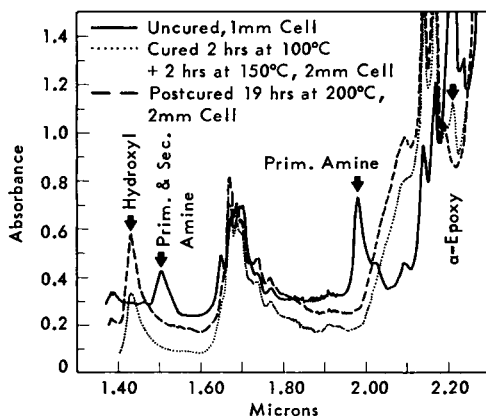


Fig. 9. Near-infrared spectra during cure of EPON X-22/CL (amine/epoxide ratio = 0.75/1).

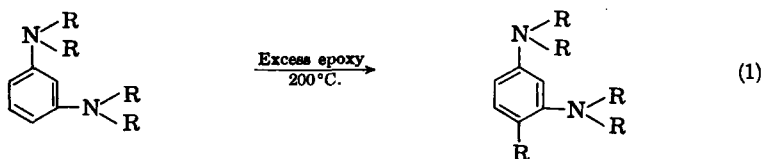
of a minor band at 2.19 μ , the disappearance of small bands at 2.23, 2.02, and 1.65 μ , and changes in the relative size of bands at 1.67 and 1.69 μ . The disappearance of the excess epoxy during postcure and the simultaneous formation of additional hydroxyl, suggests that epoxy-epoxy or epoxy-hydroxyl reactions do not occur to any great extent.

Spectral changes similar to the above were also noted for the systems EPON 828/CL and EPON X-22/*o*-phenylenediamine, both of which gave only relatively minor increases in HDT with a deficiency of the amine. Since nothing unique was noted in the spectra of the EPON X-22/CL system, it may be that the degree of completeness of cure is important, or that a minor or unknown reaction is also involved in the cure of this system.

Model Compounds

Preparation. To simplify the study of the cure, two model compounds, the adducts of CL with phenyl glycidyl ether or *n*-butyl glycidyl ether, were prepared by heating a 5/1 mole ratio mixture of the appropriate glycidyl ether and CL for 5 hr. at 100–150°C. The phenyl glycidyl ether adduct was purified by recrystallization from benzene, the *n*-butyl glycidyl adduct by distilling off the unreacted ether at 150°C./10 mm. Hg. The latter product did not crystallize. The analytical results shown in Table III indicate good agreement with theory.

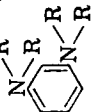
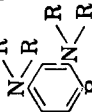
The model compounds were thermally treated at 200°C. in the presence of an added amount of the respective glycidyl ether, in the hope of achieving reaction of another epoxide according to eq. (1):



where R is $-\text{CH}_2\text{CHOHCH}_2-\text{O}-\text{C}_4\text{H}_9$, or $-\text{CH}_2\text{CHOHCH}_2-\text{O}-\text{C}_6\text{H}_5$. In the case of the phenyl glycidyl ether/CL adduct, the mixture was simply stirred together in a flask for 7 hr. The product did not crystallize from benzene and the unreacted ether was distilled off. Two thermal treatments of the butyl glycidyl ether adduct were attempted at 200°C., one for 17 hr. in a small pressure vessel, and another under reflux for 6.5 hr. In each case, less than the added amount of butyl glycidyl ether was recovered by vacuum distillation, indicating the possibility of further reaction. The changes in the elemental analyses given in Table III are in agreement.

Spectroscopic Examination. Infrared examination could not establish any change in the ring substitution upon thermal treatment. In the case of the phenyl glycidyl ether adducts, the strong monosubstituted aromatic obscured the 5–6 μ region, and the bands observed in that region for the

TABLE III
Properties of Adducts of CL with Phenyl Glycidyl Ether or *n*-Butyl Glycidyl Ether

Assumed structure	R group		C, %	H, %	N, %	O (by diff.), %	Aromatic H (NMR), %
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{R} \end{array}$ 	^a —CH ₂ —CHOH—CH ₂ —C ₆ H ₅	Found	71.4	6.8	3.84	17.8	—
		Calc.	71.2	6.8	3.95	18.1	—
	—CH ₂ —CHOH—CH ₂ —C ₄ H ₉	Found	64.8	10.1	4.35	20.8	6.4
		Calc.	65.0	10.2	4.46	20.4	6.25
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{R} \end{array}$ 	^b —CH ₂ —CHOH—CH ₂ —C ₆ H ₅	Found	70.8	7.5	2.89	18.8	—
		Calc.	71.3	6.8	3.26	18.6	—
	—CH ₂ —CHOH—CH ₂ —C ₄ H ₉	Found	64.8 ^c	10.4 ^e	3.80 ^c	21.0 ^c	7.2 ^d , 4.4 ^e , 5.5 ^e
		Calc.	64.9	10.3	3.70	21.1	3.85

^a Adducts prepared at temperatures below 150°C.

^b Adducts treated at 200°C. in presence of excess glycidyl ether.

^c After 17 hr. in pressure vessel.

^d After 1.5 hr. under reflux.

^e After 6.5 hr. under reflux.

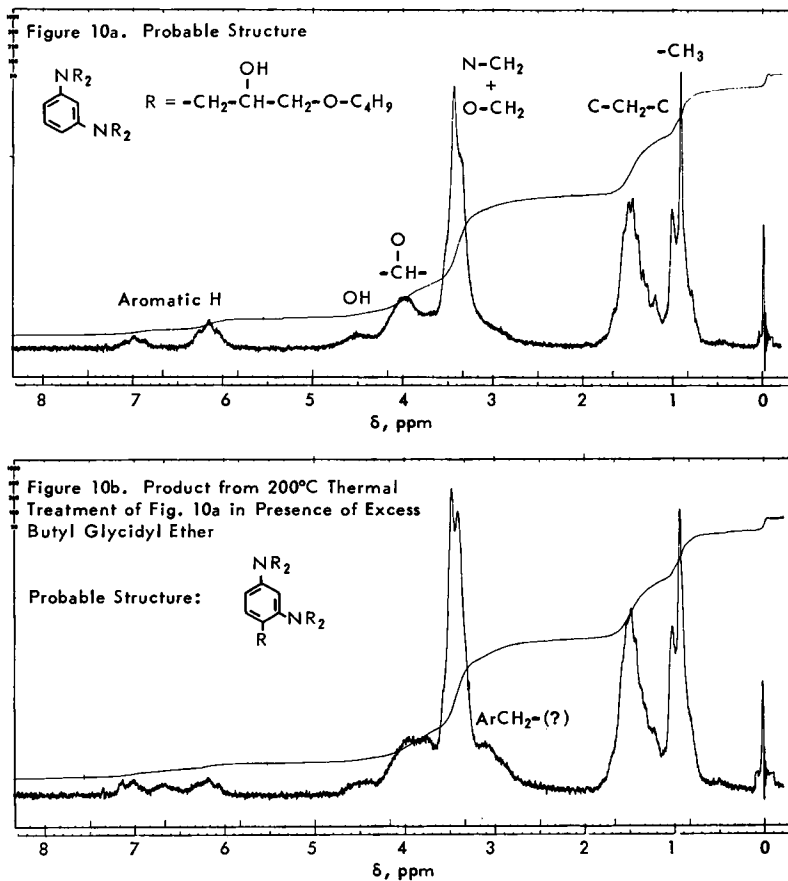


Fig. 10. NMR spectra at 60 Mc./sec. of butyl glycidyl ether/CL adduct.

butyl glycidyl ether adducts were not typical of the various di- or tri-substituted aromatics as reported by Young et al.⁵

NMR examination was able to show decreases in the amount of aromatic hydrogen after thermal treatment of the butyl glycidyl ether adduct, which would correspond to an increase in the degree of substitution of the CL ring. Before thermal treatment, the aromatic hydrogen content was 6.4%, compared to a calculated value of 6.25%, as given in Table III. Figure 10 shows the 60 Mc./sec. NMR spectra. The heated samples gave values of 5.5%, after 17 hr. in the pressure vessel, and 7.2 and 4.4% after 1.5 and 6.5 hr., respectively, under reflux, the calculated value being 3.85% for the adduct of CL with 5 moles of butyl glycidyl ether. The NMR values may be in error by $\pm 1\%$. In addition to the decrease in aromatic hydrogen, a small new peak at 3.1 ppm, which did not shift upon addition of formic acid, was observed in the NMR spectra of the thermally treated samples; this peak could be due to aromatic- CH_2 formed in the alkylation.

In the case of β -phenethyl alcohol, this band is found at 2.75 ppm, and with *o*-ethylaniline, at 2.3 ppm.

Pyrolysis-Hydrogenation-GLC Studies. Some further evidence for the reaction of a fifth epoxy group at the 4-position on the CL ring has come from pyrolysis-hydrogenation-GLC studies of the butyl glycidyl ether-CL adduct. The filament pyrolyzer of Dimbat et al.³ was used at 550°C. with a 15-ft., 10% SE 30 silicone/3% Pt/Chromosorb W column, programmed at 40–200°C. A small peak, amounting to 0.5% of the observed products through C₁₀, having the same retention time as propylbenzene, was found in the chromatogram of the thermally treated adduct. This peak was missing in the pyrolysis pattern of the normal adduct. The propylbenzene would result from thermal scission of the N substituents, the butyl ether groups and the hydroxyl, followed by hydrogenation; the ring may or may not be hydrogenated.

Discussion of New Curing Reaction

The evidence obtained from the study of the model compounds, especially the adduct of *n*-butyl glycidyl ether and *m*-phenylenediamine, indicates the strong possibility of the reaction of a fifth epoxide group with the amine. At the 200°C. temperature required, the tertiary nitrogens may activate an adjacent site, the 4-position, on the CL ring. Although the conditions, except for the high temperature, are appreciably different, some related reactions are known. A possible mechanism is for one of the reacted epoxy molecules to migrate from nitrogen to a *para* or *ortho* ring carbon, as in the Hofman-Martius rearrangement,^{6,7} followed by reaction of the newly formed secondary amine with another epoxy group. This rearrangement is normally carried out with alkyl aniline hydrochlorides in sealed tubes at 300°C. and above, but also takes place over anhydrous cobaltous chloride at 220°C.⁸ or over aluminum or titanium oxides at 400°C.⁹ The near-infrared spectra of cured resin samples, postcured without excess epoxy, did not show the reappearance of secondary amine, although this group might not be long-lived.

CONCLUSIONS

(1) Castings with heat distortion temperatures as much as 100°C. higher than the normal value of 150°C. result when certain epoxy resins of the EPON 828 type are reacted with less than the stoichiometric amount of *m*-phenylenediamine (CL) curing agent and given a severe postcure.

(2) Several glycidyl ethers of polyphenols show this effect, but the highest HDT values, about 250°C., have been obtained with special resins such as EPON X-22, a crystalline version of EPON 828, low in chlorine content and in higher molecular weight condensation products.

(3) To achieve the highest HDT values, it is necessary to post cure the samples for 12–24 hr. at 175–200°C. Longer times or higher temperatures result in a reduction in HDT to 170–190°C.

(4) To date, *m*-phenylenediamine has been the only aromatic amine to show this effect. The optimum concentration is about 75% of stoichiometric, assuming the usual functionality of four equivalents per mole. The *ortho* and *para* isomers, substituted CL, and other amines give a decrease in HDT when used under similar conditions.

(5) The stoichiometry required for maximum HDT suggests an increase in functionality of the CL, to a value of 5 eq./molecule. Evidence for the reaction of a fifty epoxy group, apparently at the 4-position of the CL ring, has been obtained by examination of model compounds, chiefly the adduct of *n*-butyl glycidyl ether and CL, by NMR and pyrolysis studies.

(6) Near-infrared spectra of cured and postcured resin castings are consistent with the proposed reaction, but such data have not been limited to the systems giving highest HDT values, suggesting a difference in the completeness of the new cure mechanism.

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Résumé

Des objets moulés présentant des températures de distorsion thermique exceptionnellement élevées sont obtenues lorsque certaines résines du type EPON-828 sont traitées et qu'environ 75% de la quantité stœchiométrique de méthaphénylènediamine sont soumises à traitement pendant 10-20 heures à 175-200°C. L'amélioration de température de distorsion à la chaleur est d'environ 10°C jusqu'à des valeurs les plus élevées. Les autres éthers glycidiques de polyphénol ont montré de phénomène à un degré moindre mais d'autres agents de traitement aminé y compris les isomères et les produits de substitution de la méthaphénylènediamine n'ont aucun effet. Une nouvelle réaction de post-traitement a été développée et mise en évidence par des études de résonance nucléaire magnétique et de pyrolyse sur des composés modèles; cette étude confirme le postulat que la méthaphénylènediamine est alcoylée par un cinquième groupe époxy au cours du post-traitement, vraisemblablement à un carbone du noyau aromatique avec comme résultat un pontage accru.

Zusammenfassung

Gussstücke mit unerwartet hohen Hitzeverformungstemperaturen werden erhalten, wenn gewisse vorbehandelte Harze vom Typ EPON 828 und 75% der stöchiometrischen Menge von *m*-Phenylendiamin durch 10–20 Stunden bei 175–200°C nachgehärtet werden. Die Verbesserung der Hitzeverformungstemperatur betrug etwa 100°C, bis zu Werten von 250°C. Ein rekristallisiertes Harz liefert die höchsten Werte. Andere Glycidyläther von Polyphenolen zeigten dieses Phänomen in einem geringeren Grad, während andere Aminhärter, darunter Isomere und Substitutionsprodukte von *m*-Phenylendiamin, keinen Einfluss hatten. Gewisse Hinweise auf eine neue Härtingsreaktion wurden durch NMR- und Pyrolyseuntersuchungen von Modellverbindungen erhalten; es scheint, dass das *m*-Phenylendiamin während der Nachhärtung vermutlich an einem Ringkohlenstoff, mit einer fünften Epoxygruppe alkyliert wird, was zu einem höheren Vernetzungsgrad führt.

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