Some Correlations between Mechanical Properties and Structure of Epoxy Resin Castings

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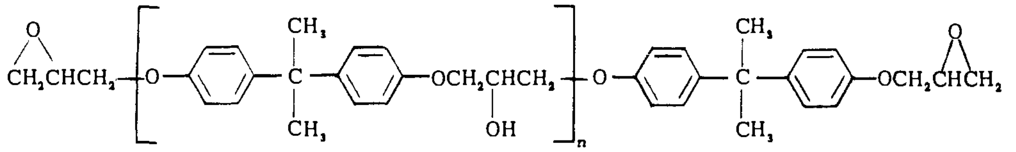
Epoxy resins represent a class of synthetics which has gained ready acceptance during the past 10 years. Most of these resins are prepared from bisphenol A and epichlorohydrin and can be represented by the general formula:



These materials can be divided into two broad classes: First, the solid resins, which are used principally in coatings applications, and which have *n* values ranging approximately from 1 to 20. Second, the liquid resins, which find their greatest use in structural plastics applications, and which are prepared in such a way that *n* is as close to 0 as possible. Some idea of the potential of the liquid resins in reinforced plastics, castings, and adhesives applications were presented in the form of case histories by Zolin and Green (*13*).

These lower molecular weight, viscous liquid epoxy resins are used in conjunction with appropriate catalysts and/or hardeners. Catalysts for epoxy resins can be defined as compounds that can cause the glycidyl ether group to self-polymerize. Hardeners, on the other hand, are polyfunctional compounds having groupings that are reactive toward the glycidyl type of epoxide and that combine with epoxy resins in stoichiometric or near-stoichiometric ratios. The more commonly used hardeners are polyamines, polybasic acids or their anhydrides, and polyphenols.

Previously published work from these laboratories (*11,12*), in which the model compound reactions of glycidyl ethers were studied, has given an indication of the chemical reactions taking place during the curing of epoxy resin systems. If one can extrapolate from these model studies to the gelled, completely immobile systems of commerce, conclusions might even be drawn regarding the speed and degree of cure of specific epoxy resin-hardener combinations made under a given set of conditions. Nothing in this treatment, however, will predict the physical properties of the cured system. Whether a given epoxy resin-hardener combination will show the characteristics needed for a specific application has had to be determined more or less empirically.

Over the past several years, however, literally hundreds of epoxy resin-hardener systems have been tested in Bakelite's laboratories. From the amassed data, some generalizations about the influence of chemical architecture on physical properties have been drawn.

By way of orientation, the properties of a typical unfilled casting, made from the low molecular weight type of bisphenol A-epichlorohydrin resin and a polyalkylene polyamine hardener, are given in Table I. These properties might be described as indicating a good balance of strength and toughness. In addition, such a material has good electrical properties and fairly good chemical resistance. One limitation, however, is indicated by the moderate heat distortion temperature of 100°C. It has been found that strength values and electrical properties of such castings fall off rapidly at temperatures near 100°C. Heat distortion temperature data, therefore, have been used as necessary, but partial, guides in screening new epoxy resin-hardener combinations.

In a detailed investigation of the epoxy resin-polyalkylene polyamine hardener system, it was found that the functionality of the amine hardener has a definite, but limiting, effect on heat distortion temperature. Table II, illustrating this effect, shows the performance of the same epoxy resin described in Table I, but with polyamines having functionalities varying from 3 to 42. This effect correlated well with the functionality of the system as a whole, calculated according to the definition of the term as originated by Carothers (*3*). With the aid of this concept, it can be shown that a hardener having an infinite functionality would not raise the functionality of the system beyond the limiting value of 4.

As might be expected, lengthening of the alkylene chain between the amine functions of a diamine hardener from two to six carbon atoms had the effect of lowering the heat distortion temperature. Table II also shows an almost identical effect from a six carbon-atom chain as from a hetero-atom chain of similar length. On the other hand, the inclusion of aromatic rings in the hardener structure had a marked effect in increasing the heat distortion temperature. Another advantageous feature of aromatic hardeners was found in a much improved resistance to ketone and chlorinated solvents. Bishop (*1*) has recently indicated that aniline-formaldehyde resins are superior to the aliphatic polyamines as epoxy resin hardeners. That cycloaliphatic polyamines perform in a manner similar to aromatic polyamines was inferred from the data recorded using a diaminomenthane and aminoethylpiperazine (see Table II). A beneficial effect of symmetry in the hardener was implied by a comparison of the isomeric amines triethylenetetramine and triaminoethylamine.

Structural features of the epoxy resin also play a part in determining the properties of an epoxy resin casting. One

Table I. Strength and Other Mechanical Properties of Unfilled Castings[a] of ERL-2774[b]/ERL-2793[c]

		ASTM Test
Heat distortion temp., °C.	100	D 648-45T
Tensile strength, p.s.i.	8,500	D 638-52T
Flexural strength, p.s.i.	16,000	D 790-49T
Flexural modulus of elasticity, p.s.i.	450,000	
Compressive strength, p.s.i.	36,000	D 695-54
Compressive yield, p.s.i.	18,000	
Izod impact strength, ft.-lb./inch	0.2	D 256-54T
Rockwell hardness, M	105	D 785-54

[a] Made by mixing resin and hardener quickly at room temperature, deaerating by applying a partial vacuum, and pouring carefully into a mold consisting of two parallel polished steel plates separated by suitable gaskets and spacers. The resin mix was allowed to stand in the mold 1 hour at room temperature, then placed in a 50°C. oven for 2 hours and finally in a 80°C. oven for 4 hours. After cooling, the casting was removed from the mold and given a 3-hour postcure at 120°C. ASTM pieces were obtained by machining.

[b] Low molecular weight bisphenol A-epichlorohydrin type of epoxy resin having an epoxide equivalent weight of 185-200.

[c] Viscous liquid polyalkylene polyamine-based hardener containing an amino-hydrogen equivalent weight of about 40. A weight ratio of 25 parts of hardener to 100 parts of resin represents a stoichiometric ratio and was the ratio employed to obtain the data reported here.

Table II. Curing of ERL-2774 with Amine Hardeners of Different Functionalities

Amine hardener[a]	Functionality[b] Amine	Functionality[b] System	Heat Dist. Temp., °C.	Flexural Strength, P.S.I.
Aliphatic				
ZZL-0803[c]	3	2.4	55	13,500
Ethylenediamine	4	2.7	90	16,000
Diethylenetriamine	5	2.8	95	16,000
Triethylenetetramine	6	3.0	102	17,500
Polyethyleneamine 1200[d]	29	3.7	108	14,000
Polyethyleneamine 1800[d]	42	3.8	106	16,000
Limit		4.0	110(est.)	...
Tri(aminoethyl)amine	6	3.0	127	15,000
Hexamethylenediamine	4	2.7	75	...
bis(2-Aminoethoxy)dimethyl silane	4	2.7	75	16,000
Cyclic				
m-Phenylenediamine	4	2.7	135	17,000
p-Phenylenediamine	4	2.7	135	17,000
Benzidine	4	2.7	150	17,000
4,4′-Methylenedianiline	4	2.7	145	17,000
o-Tolidine	4	2.7	135	17,000
1,8-Diaminomenthane	4	2.7	143	15,000
Aminoethylpiperazine	3	2.4	102	18,600

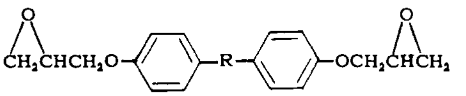
[a] All hardeners were mixed with epoxy resin in the calculated stoichiometric proportion. The aliphatic amine-hardener materials were cured 1 hour at room temperature, 2 hours at 50°C., 4 hours at 80°C. and finally 3 hours at 120°C. Aromatic amine-hardener materials were cured 16 hours at 80°C., 3 hours at 120°C. and 2 hours at 160°C.

[b] Amine functionality is identical to number of amino hydrogens in polyamine molecule. System functionality is calculated by definition [see (*3*)]: total number of functions employed in curing reaction divided by number of molecules involved.

[c] Dicyanoethylated diethylenetriamine.

[d] These polyethylene amines were obtained from Union Carbide Chemicals Co., Division of Union Carbide Corp., and were compounds having formula $H_2N(C_2H_4NH)_nH$ and average molecular weights as indicated.

Table III. Influence of Connecting Link in Bisphenol-Based Epoxy Resins



Castings were made from 1.25 moles of epoxy resin plus 1.00 mole of parent bisphenol along with 0.4% KOH as a catalyst. Curing was at 65°C. for 16 hours, plus 3 hours at 100°C. and 3 hours at 120°C.

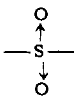
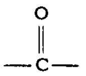
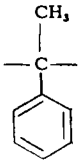
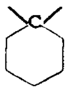
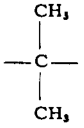
—R—	Softening Temp., °C.
 $-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-$	180
 $-\overset{\overset{O}{\parallel}}{C}-$	160
	135
	135
 $-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-$	100
$-CH_2-$	85

Table IV. Methylenedianiline-Cured Epoxy Resins Based on Tetrachlorobisphenol A and Bisphenol A

Property	Tetrachlorobisphenol Resin	Bisphenol Resin (ERL-2774)
Mechanical Properties of Unfilled Castings[a]		
Flexural strength, p.s.i.	1.2×10^4	1.5×10^4
Flexural modulus, p.s.i.	4.0×10^5	3.7×10^5
Izod impact strength, ft.-lb./inch	0.23	0.25
Heat distortion temp., °C.	168	133
Rockwell hardness, M scale	102	105
Flammability	Self-extinguishing	Supports combustion
Flexural Strengths and Moduli of Glass Cloth Laminates[b]		
25°C. strength, p.s.i.	9.1×10^4	8.4×10^4
25°C. modulus, p.s.i.	4.0×10^6	3.8×10^6
150°C. strength, p.s.i.	6.6×10^4	4.5×10^4
150°C. modulus, p.s.i.	3.8×10^6	3.0×10^6

[a] Each epoxy resin was hardened with calculated stoichiometric quantity of methylenedianiline, using cure cycle of 3 hours at 90°C., 3 hours at 110°C., and 1 hour at 200°C.

[b] Laminates were made from No. 181 glass cloth, Volan (Du Pont) A finished, and contained about 32% resin. Glass cloth was first preloaded in a treater from a toluene-acetone solution, the resin-hardener combination being advanced on the glass cloth by heating for about 10 minutes at 140°–150°C. One-eighth inch laminates were prepared by pressing 12 parallel plies of treated stock at 160°C. for 1 hour at 1000 p.s.i. pressure. Bisphenol resin laminates were post cured for 6 hours at 200°C., tetrachlorobisphenol resin laminates at 160°C. for 6 hours.

Table V. Effect of Bisphenol Orientation on Performance of Epoxy Resins in Castings

	Di(hydroxyphenyl)-methane[a]			Bisphenol A[b]
Isomer	2,2′	2,4′	4,4′	4,4′
Heat distortion temp., °C.	75	74	81	85
Izod impact strength, ft.-lb./inch	0.3	0.5	3.0	1.5
Flexural strength, p.s.i.	16,000	21,000	14,000	16,000
Flexural work to break, (ft.-lb.) ¼ × ½ × 4 inches	1.1	6.7	9.4	5.7

[a] Diglycidyl ethers cured with parent diphenols in ratio of 1.25 epoxide groups to 1.00 phenolic hydroxyl, with 0.4% KOH catalyst. Cure cycle was 16 hours at 65°C., 3 hours at 100°C., and 3 hours at 120°C.

[b] Diglycidyl ether of bisphenol A was cured with bisphenol A in manner noted above.

example of this is shown in Table III, which lists the softening temperatures of some bisphenol diglycidyl ether resins cured with their parent bisphenols (so as to magnify the contribution of the connecting link —R— to this property). The appreciable differences in softening temperature found suggest that these moities make for improved resistance to deformation at elevated temperatures in the ascending order of Table III.

The high position of the sulfone linkage in this listing is thought to be due to its high order of polarity. The introduction of polarity in other ways had a similar effect. For example, the tetrachloro derivative of bisphenol A was made into a diglycidyl ether having distinctly better heat distortion performance than the commercial epoxy resins. Table IV gives a comparison of unfilled castings and glass cloth laminates made from the diglycidyl ethers of tetrachlorobisphenol A and of bisphenol, hardening in each case with the stoichiometric amount of methylenedianiline. Similarly, the chlorinated hardener HET (Hooker Electrochemical Co. trade-mark for hexachloroendomethylene tetrahydrophthalic anhydride) anhydride yielded a casting with higher heat distortion temperature (199°C.) than phthalic anhydride (132°C.) when compared in stoichiometric ratios with a tertiary amine catalyst with the same liquid epoxy resin. The effect was also reported by Robitschek and Nelson (*10*) for the same systems in a different combining

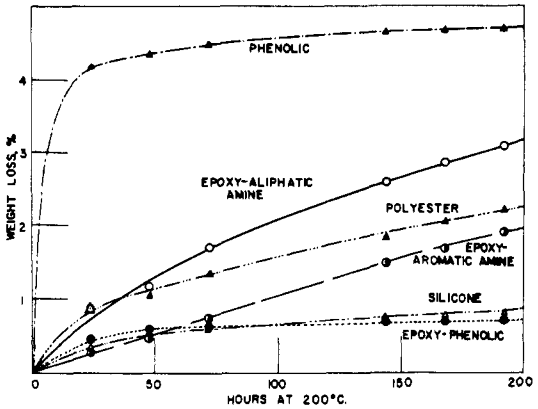


Figure 1. Weight loss at 200° C. of disks, 2.25 inches in diameter × 0.25 inch thick, of experimental epoxy resin castings, phenolic casting, unsaturated polyester-styrene casting, and silicone polymer

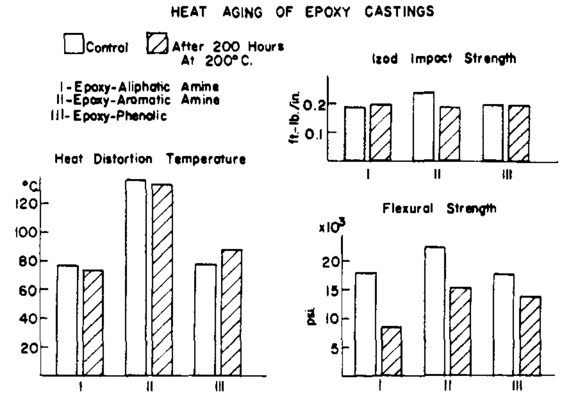


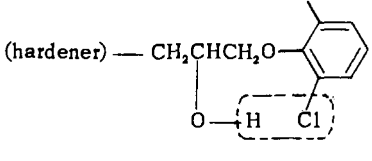
Figure 2. Heat distortion temperatures, room temperature flexural strengths, and room temperature impact strengths of three types of epoxy resin castings before and after 200 hours of continuous exposure to 200° C.

ratio and cured without a catalyst (in which case a somewhat different curing mechanism operates). This interesting effect of chlorine suggested that chlorinated polyaromatic amines might prove to be superior epoxy hardeners. Some chlorinated methylene dianilines prepared in the author's laboratory, however, were so feebly basic that curing of epoxy resins with them became an extremely sluggish process.

Para linkages in epoxy resins appeared to be more desirable than ortho, with differences showing up in toughness rather than in heat distortion or in strength. Table V shows some properties of the isomeric 2,2',2,4', and 4,4'-di(hydroxyphenyl)methane series of glycidyl ethers hardened with their parent diphenols. Toughness is represented by Izod impact strength and by flexural work-to-break (the latter being the area under the flexural strength test stress-strain curve).

As a direct consequence of the limitation imposed on the functionality of an epoxy resin-hardener system by the resin functionality, it would be predicted that a higher functional glycidyl ether would have certain advantages over the conventional bisphenol A diglycidyl ethers. Some indication of this has been published. For example, Dearborn, Fuoss, MacKenzie, and Shepherd (*4*) have reported higher "thermal yield points" from polyglycidyl ethers such as those made from tetraphenols derived from diketones and phenol. Phenol-formaldehyde novolak resins, without question a more practical class of intermediate, have been suggested as epoxy resin bases by several authors (*2*, *6–9*).

In addition to the requirement that an epoxy resin-hardener combination show a high heat distortion temperature, it is also imperative that the system be stable to extended exposure at such temperatures. A few systems showed high heat distortion temperatures and interesting strength properties at elevated temperatures but decomposed on prolonged heating. An example of this type of thermal instability was found in castings based on the diglycidyl ether of tetrachlorobisphenol A. (Decomposition in this case was thought to involve a dehydrochlorination mechanism. It was also found that this aromatic chlorine was abstracted by dilute caustic under very mild conditions. Both types of decomposition were thought to be facilitated by the peculiar position of chlorine relative to hydroxyl in the cured, or hydrated, product:



This instability was not found in the tetrachlorobisphenol A, itself, or in its dimethyl ether.)

The problem of heat stability of epoxy resin-hardener castings was investigated more generally by weight loss experiments at 200°C. Figure 1 summarizes the weight loss–time at 200°C. relationship found in the case of some selected epoxy resin-hardener systems along with a few controls consisting of more familiar thermosetting plastics. Outstanding in the epoxy materials tested were certain combinations employing polyphenols (phenolformaldehyde Novolak resins) as hardeners. These were comparable in weight loss to a silicone material and, apparently, to certain epoxy resin-pyromellitic dianhydride systems recently reported by Feild and Robinson (*5*). The effect of heat-aging on epoxy castings was further checked by comparing detailed (room temperature) mechanical strength data before and after a 200-hour continuous exposure to 200°C. The data shown in Figure 2 are suggestive of some degradation on heating when polyamines were employed as hardeners and of less degradation and perhaps even some continuation of cure in the case of phenolic hardeners.

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