Reactive Diluents in Aromatic Amine-Cured Epoxy Adhesives

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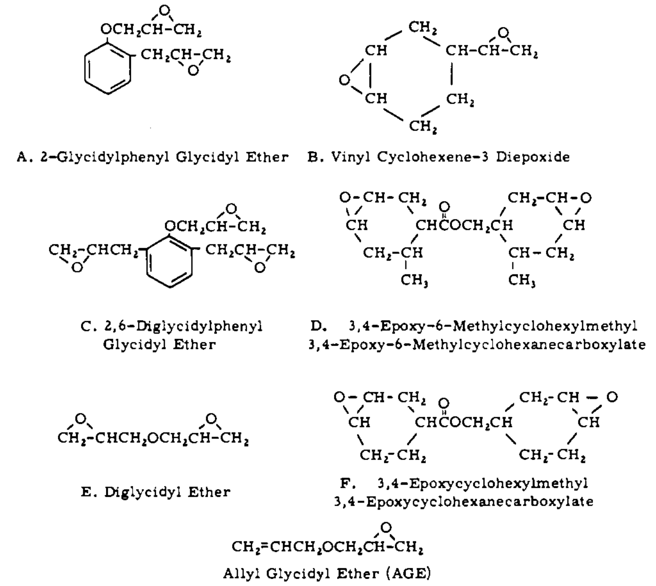
THE ELEVATED temperature properties of an epoxy resin system depend to a large degree on the cross-linking density. To improve the handling characteristics of paste adhesives, the formulator sometimes finds it necessary to use various diluents to control the viscosity of the system. One method is to employ solvents or plasticizers. These materials, however, even in small amounts, greatly reduce the elevated temperature bond strength. This can be largely avoided by using diluents which contain epoxy groups. The diluent can thus become chemically bound in the cross-linked resin system and the effect on elevated temperature bond strength is minimized. This article reports the results of a study on the effects of chemical structure and epoxy functionality of various epoxide-containing diluents in aromatic amine-cured paste adhesives. Since rather arbitrary concentrations were used, the results reflect the relative value of the various diluents but do not necessarily represent optimum formulations.

The chemical structure and name of the diluents studied are shown in Figure 1. They are referred to hereafter as A, B, C, D, E, F, and AGE. Most of these are experimental materials having a variety of different types of epoxide groups. These include aromatic and aliphatic glycidyl ethers, glycidyl groups, an epoxyethyl group, and epoxycyclohexyl groups. All the compounds are potentially toxic or hazardous chemicals. In general the toxic nature of epoxides is dependent on molecular weight, volatility, and the reactivity and concentration of the epoxide groups.



A. 2-Glycidylphenyl Glycidyl Ether

B. Vinyl Cyclohexene-3 Diepoxide

C. 2,6-Diglycidylphenyl Glycidyl Ether

D. 3,4-Epoxy-6-Methylcyclohexylmethyl 3,4-Epoxy-6-Methylcyclohexanecarboxylate

E. Diglycidyl Ether

F. 3,4-Epoxycyclohexylmethyl 3,4-Epoxycyclohexanecarboxylate

Allyl Glycidyl Ether (AGE)

Figure 1. Chemical structure and names of the diluents

Of all the compounds shown, only allyl glycidyl ether (AGE) contains one epoxide group per molecule. Monofunctional diluents such as this tend to reduce bond strength at elevated temperatures. Once this compound has reacted with amine hydrogen it terminates the growth of the polymer chain in that direction and thus the cross-linking density of the system is reduced. This effect can be demonstrated experimentally, as is shown in Figure 2. As various percentages of allyl glycidyl ether were used to replace the diglycidyl ether of bisphenol A (Epon 828) in an aromatic amine-cured casting, the heat distortion temperature was markedly reduced. Figure 3 shows that the functionality of the diluent also has a definite effect on the bond strength at elevated temperatures. The monofunctional diluent (AGE) reduced bond strength at elevated temperatures even in low concentrations. However, if a polyfunctional diluent, such as A, is used, the elevated temperature bond strength appears to be unaffected. Additional measurements of this effect as well as pertinent experimental details are shown in Table I.

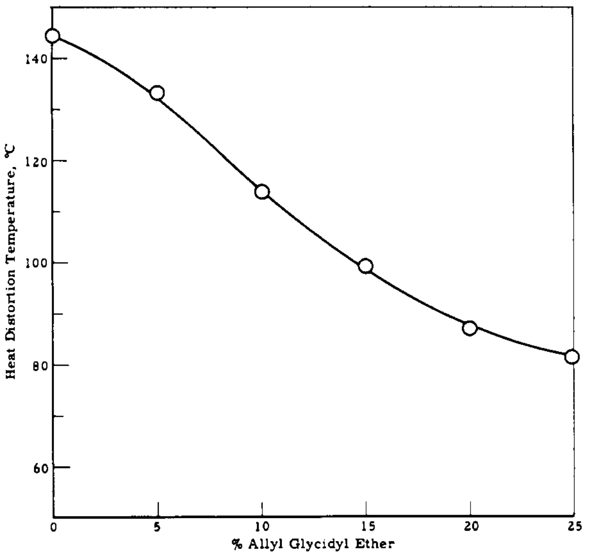


Figure 2. A monofunctional diluent reduces the heat distortion temperature of Epon 828

EXPERIMENTAL

The tensile shear measurements were made on aluminum-to-aluminum lap shear coupons prepared by using clad 2024-T3 alloy, 0.064 inch thick. The metal was prepared for bonding as follows:

The aluminum was thoroughly degreased in a Blakeslee self-distilling degreaser, Model R. The degreasing fluid was stabilized trichloroethylene. The bonding surfaces were submerged for 20 minutes at 150° to 160° F. in an etching solution consisting of distilled water, 65.5 parts (wt.) sodium dichromate, 7.5 parts (wt.) and concentrated sulfuric acid,

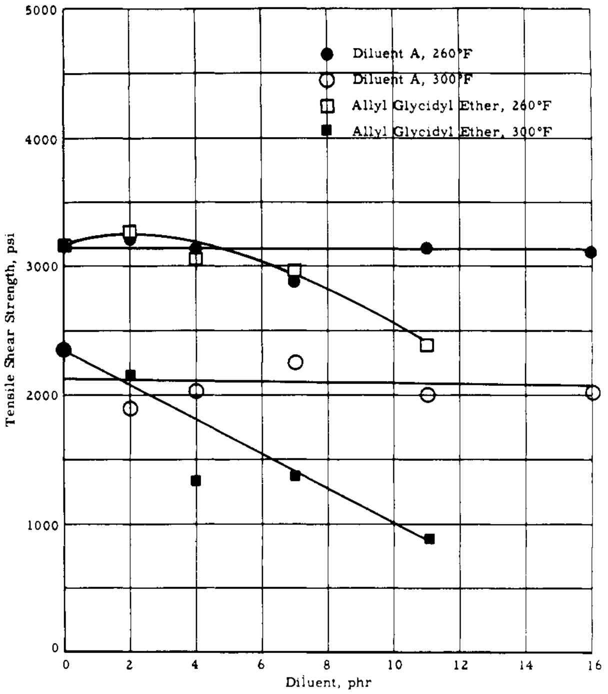


Figure 3. A monofunctional diluent (AGE) reduces bond strength; a difunctional one (A) does not

27 parts (wt.). On completion of the etch the metal was thoroughly rinsed with tap water. Following this the panels were dried in a forced-draft oven at 150° F. for ½ hour.

Etched panels (4 × 14 inches) were used. The adhesive was applied along the long direction of the panel on the etched surface, inward from the edge approximately ¾ inch, and spread to a uniform thickness by use of a 5-mil doctor blade. Two such panels were prepared and laid face to face to give a ½-inch overlap. The assembly was held in place by U-shaped spring tension clamps until curing was complete. Curing was carried out in forced-draft ovens at the temperatures indicated in the tables. On completion of the cure the panel was cut into strips 1 inch wide by a band saw. This gave 12 lap-shear coupons with a bonded area of ½ × 1 inch. Tensile shear measurements were made on a Baldwin Southwark Tate-Emery test machine. At least six tensile shear coupons were broken for each test condition described. Since the bond area was only ½ square inch, the test value obtained in tensile shear determinations was multiplied by two. The coupons as well as the actual tests on any given formulation were selected using randomization techniques. Throughout this study the adhesive formulations used were kept as simple as possible and should not be considered necessarily as optimum mixtures or commercially practical formulations. They were used merely for determining the relative value of the diluents. Asbestos floats, for instance, was the only filler used. The only epoxy resins used other than the diluents were Epon 828, the diglycidyl ether of bisphenol A, and Epon 1031, which is essentially a tetraglycidyl ether of tetraphenol ethane. It is possible that many of these diluents could be more effectively used in combination with other epoxy resins, with other types of fillers, or at different concentrations.

Table I. Effect of Diluent Functionality on Bond Strength

Phr AGE[a]	Curing Agent Phr[b]	Temp., Room	180° F.	260° F.	300° F.
		Tensile Shear Value at[c]			
0	14.1	3190	3060	3150	2330
2	15.2	3160	3560	3250	2140
4	15.7	3640	3870	3020	1420
7	16.6	3970	3880	2960	1460
11	17.5	3970	4210	2380	880
A[a]					300° F.
2	14.6	3310	3180	3190	1876
4	15.0	3330	3200	3120	2010
7	15.7	3360	3380	2840	2240
11	16.7	3180	3360	3110	1990
16	17.8	3310	3640	3090	2000

[a] Basic formulation based on Epon 828 containing 30 phr asbestos floats, 6 phr poly(vinyl acetate) and diluent as shown.

[b] Curing agent *m*-phenylenediamine (Allied Chemical Corp.), added in amounts equivalent to epoxide content of system (diluent plus Epon 828.) Cure ½ hr. at 240° F. plus 3½ hr. at 330° F.

[c] Measured on 2024-T3 clad aluminum lap shear coupons, bond area ½ × 1in., results in p.s.i.

Basic Formulations. Although, for evaluating the diluents, as simple a system as possible was used, diglycidyl ether of bisphenol A (Epon 828) alone in combination with these materials gave adhesives which were much too thin for proper handling. High molecular weight, compatible, high-melting, thermoplastic resins could have been used to control the viscosity of the paste, but would probably lower the elevated temperature bond strength. Higher molecular weight homologs of the diglycidyl ether of bisphenol A—e.g., Epon 1009—should have a similar effect. These additions would thus have made it much more difficult to assess the relative value of the diluents. Equal weight mixtures of Epon 1031 and the diluents, however, had viscosities about equal to that of Epon 828. This afforded a means of getting practical paste viscosities while using relatively large amounts of diluents, since Epon 1031 would not lower the cross-linking density. It was necessary, however, to establish the optimum ratio of the Epon 1031-diluent mixture and Epon 828.

Figure 4 summarizes results of these experiments. This is a plot of bond strength at room temperature and at 300° F.

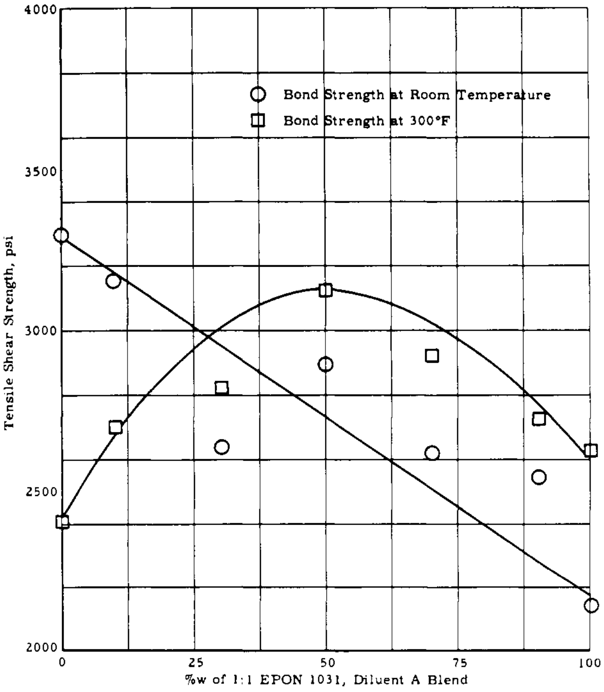


Figure 4. A 1 to 1 diluent blend–Epon 828 combination gave the maximum bond strength

as a function of the percentage of the diluent A–Epon 1031 mixture used in combination with Epon 828. The filler was 30 phr of asbestos floats. The curing agent concentration was chemically equivalent to the epoxide value of the resin system. Bond strength at room temperature decreased linearly as the diluent mixture was increased. The best bonds at 300° F. were obtained with equal weights of the diluent mixture and Epon 828. On this basis Epon 828, Epon 1031, and diluent in the ratio of 50 to 25 to 25 were chosen as the basic formulation.

RESULTS AND DISCUSSION

In the region of the heat distortion or glass transition temperature polymers change from the glassy to the rubbery or elastomeric state. In the elastomeric state a polymer should be capable of relieving internal strains due to changes in temperature (*1*, *6*). When an adhesive bond is cooled down after curing at an elevated temperature, strains develop on cooling below the glass transition temperature (*2*, *3*). These strains would contribute weakness to a bond and cause lower ambient temperature bond strengths (*4*, *5*). A resin system with low heat distortion temperature would be expected to have better bond strength at room temperature then one with a high heat distortion temperature. Conversely, a high heat distortion temperature should be a prerequisite for good bond strength at elevated temperatures, since generally a polymer has much greater strength in the glassy than the rubbery state.

Figure 5 summarizes the bond strengths obtained using the various diluents in aromatic amine-cured systems. The tensile shear measurements shown were made on coupons which had been postcured for 16 hours at 300° F. This long postcure was necessary to give a true picture of the relative merits of the materials tested. Certain of the epoxy compounds contain epoxide groups which react very slowly with aromatic amine-curing agents. This conclusion is borne out by the data in Table II, which shows that elevated temperature bond strength was improved in every case by the long postcure. Examination of both Figure 5 and Table II shows that both chemical structure and functionality influence the bond strength under the various test conditions.

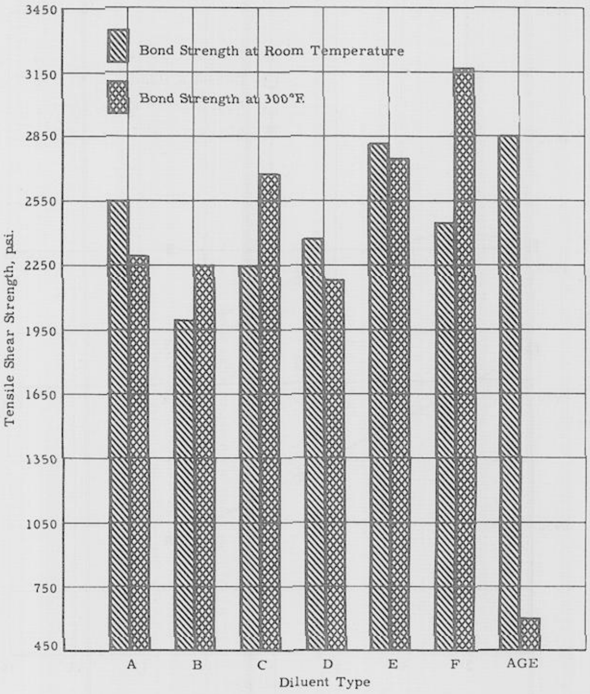


Figure 5. Bond strengths at both room temperature and 300° F. vary with the type of diluent used

Table II. Effect of Postcure on Tensile Strengths of Epon 828/Diluent Adhesive System

Diluent Type	Curing Agent Z[a] Phr[b]	Postcure,[c] Hr. at 330° F.	Temp., Room Tensile Shear Value, P.S.I.	Temp., 260° F. Tensile Shear Value, P.S.I.	Temp., 300° F. Tensile Shear Value, P.S.I.	Temp., 400° F. Tensile Shear Value, P.S.I.	Relative Effect on Viscosity[d]
A	18.0	3	2540	3130	1740	430	6
		16	2550	3180	2300	640	
B[e]	24.5	3	2290	2900	1190	400	2
		16	2100	3190	2220	520	
C	18.2	3	2990	2840	2610	480	7
		16	2240	2970	2670	620	
D	16.6	3	2410	3340	1020	490	4–5
		16	2380	3500	2180	660	
E[f]	22.6	0	2680	2940	2000	600	3
		3	2550	2820	2490	650	
		16	2810	2470	2740	860	
F[f]	16.5	3	2570	3550	2240	370	4–5
		16	2440	3200	3160	970	
AGE	18.2	0	2770	380	400	. . .	1
			2950	770	490	. . .	
		16	2850	1020	600	. . .	

[a] Liquid aromatic diamine manufactured by Shell Chemical Corp., weight per amine hydrogen 39.4.

[b] Based on total weight of adhesive formulation.

[c] Before postcure samples cured ½ hr. at 240° F. plus ½ hr. at 330° F.

[d] Effect varies from 1, greatest effect of viscosity to 7, least effect.

[e] Union Carbide Corp., Chemical Division.

[f] U.S. Patent 2,716,123.

Allyl glycidyl ether (AGE), the only monofunctional diluent evaluated, appears to fit the above hypothesis. The resin system containing AGE would undoubtedly have the lowest heat distortion temperature of any member of the series. The results show that bond strengths at elevated temperatures were low, but room temperature strength was excellent.

Table III shows the heat distortion temperatures and the theoretical number of amine-epoxide linkages possible when A,C, and diglycidyl ether (E) are cured with an aromatic diamine. The adhesive containing E gives the best room temperature bond strength, followed by A and then C. The above-mentioned hypothesis again appears to fit in the case of C *vs.*A or diglycidyl ether. The fact that diglycidyl ether is better than A is probably due to the inherently better flexibility of the aliphatic ether backbone chain. Comparison of the elevated temperature strength of these diluents, however, is much more complicated. The data shows that E gives greater 300° F. bond strength than A.

This leads to two possible explanations: A high degree of cross linking is a more important contributor to bond strength at elevated temperatures than a high heat distortion temperature, or both systems are being tested in the region above the glass transition temperature and the one containing E is a better elastomer. Bond strengths of the trifunctional epoxide C, and diglycidyl ether at 300° F. are nearly equal. Unfortunately, the heat distortion temperature for the resin system containing C is not available; however, it can be assumed greater than 300° F. since it is known that C (cf. Table III), Epon 828 and Epon 1310 individually give heat distortion values equal to or greater than 300° F. when cured with an aromatic diamine. The first explanation would best fit this case.

Diluent F gave the best performance at elevated temperatures of any member of the series. Comparison with diluent D shows that the substituent methyl groups had a great influence on elevated temperature bond strength. These substituent methyl groups would not be expected to have such a profound effect. To determine if this could be due to the rate of reaction with the aromatic amine, model rate

Table III. Heat Distortion Temperatures and Number of Epoxy-Amine Linkages[a]

Diluent	Amine-Epoxide Linkages, Equiv./100 g.	Heat Distortion Temp., ° C.
A	0.754	134
E	1.087	133
C	0.885	180.5

[a] Heat distortion temperatures and calculations based on the compounds cured with *m*-phenylenediamine (no other epoxides present).

experiments were performed. The results are shown in Figure 6. Aniline was used, since it gives essentially a linear polymer permitting the reaction to be following for a longer period of time. The data show that D has a lower rate of reaction; this could decrease the rate of same which could account for the lower bond strength at elevated temperatures. All of the compounds containing an epoxycyclohexyl group (B, D and F) required long cures to attain good 300° F. bond strength (cf. Table II). This indicates that the epoxycyclohexyl group in general cures slowly with aromatic amines.

Since (*B*) gives lower elevated temperature strengths than F, it would appear that the epoxyethyl group cures rather slowly also.

Diluents E and F appear to be of nearly equal value. Diglycidyl ether did not perform quite as well at the high temperatures, but was more effective in decreasing the viscosity of the paste, and gave a much faster cure and better bond strength at room temperature. Diluent C was similar to diglycidyl ether in high temperature tensile shear properties. It did not, however, reduce the viscosity as effectively, and room temperature behavior indicated greater brittleness in the bonds. Diluents A, B, and D appear to be of nearly equivalent value, with A giving somewhat better bonds at room temperature and a faster cure.

Improvement of Room Temperature Bond Strength. All of the diluents tested appeared to give rather brittle bonds as characterized by low room temperature bond strengths. One of the methods commonly used to improve bond strength at room temperature is through the incorporation of tough, high-melting thermoplastic resins. Two of the more commonly used resins, poly(vinyl acetate) and poly(vinyl formal), were briefly examined with the diluent A formulation, to test the feasibility of this approach. Only one concentration of the additive was used in each case. Based on previous experience 6 phr of poly(vinyl acetate) and 20 phr of poly(vinyl formal) were used. Although these are not necessarily optimum quantities, they indicate possibilities of this approach. The data are summarized in Table IV.

Poly(vinyl formal) was not very promising. The increase in bond strength at room temperature was negligible and the bond strength at 300° F. was markedly reduced. Poly(vinyl acetate), however, may be worthy of further investigation. Some improvement in room temperature bond strength was noted, and although there was some loss at the intermediate temperature, there was a definite increase in bond strength at 300° F.

CONCLUSIONS

Present data suggest that reactive diluents can be used to control viscosity and improve handling characteristics of aromatic amine-cured adhesive systems. The monofunctional diluent can only be used if high temperature properties are not important. A polyfunctional diluent gives high cross-linking density and good high temperature strength but causes some loss in room temperature bond strengths, The merit of the diluents, in order of decreasing effectiveness taking all factors into consideration, is: E, F, C, A, D = B. Diluent E is more valuable than F by reason particularly of its faster cure rate.

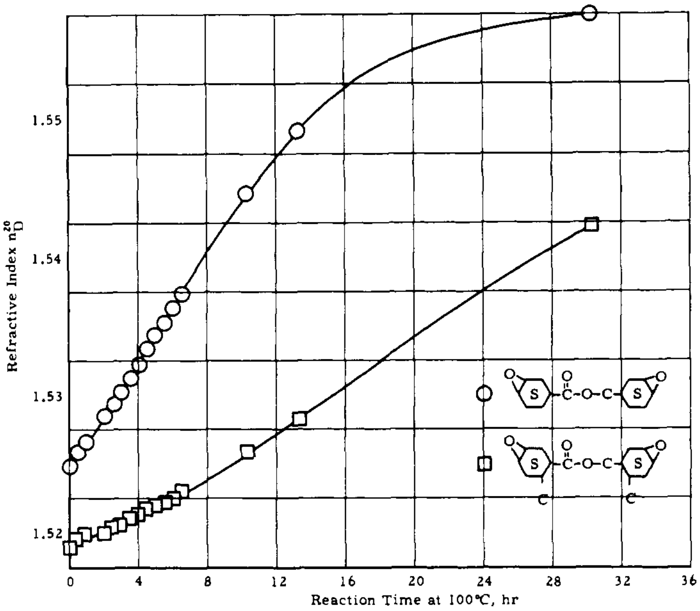


Figure 6. The presence of methyl groups greatly reduces the rate of reaction of cyclohexyl epoxides with aniline

Table IV. Effect of Thermoplastic Resins on Bond Strength[a]

Thermoplastic Added	Phr	Temp.,			
		Room	260° F.	300° F.	400° F.
		Tensile Shear Value, P.S.I.			
None	0	2540	130	1740	430
Poly(vinyl acetate)[b]	6	2850	2760	2440	440
Poly(vinyl formal)[c]	20	2660	2680	1300	480

[a] Evaluation made using the basic formulation containing diluent A. Postcure 3 hr. at 330° F.

[b] Vinylite Resin AYAF, Bakelite Corp.

[c] Formvar 15/95E, Shawinagan Resins.

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