

Hydrolytic Stability of Some Uncured Epoxy Resins*

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Synopsis

The hydrolytic stability of triglycidyl(4-aminophenol) (ERL 0500), tetraglycidyl(methylene-dianiline) (MY720), and a number of model compounds has been investigated. It has been shown that at 60°C and 96% relative humidity undiluted *N*-glycidyl aromatic amine-based epoxy resins readily undergo hydrolysis followed by homopolymerization. Impurities in the resin may significantly accelerate the rate of reaction. The effect of the consequent loss of epoxide on the performance of an adhesive based on ERL 0500 has been studied. The high-temperature tensile-shear strength of joints was markedly reduced when the adhesive was aged, before cure, for 24 hr at 60°C and 96% relative humidity. Some implications of these findings for aerospace applications of epoxy compounds are discussed.

INTRODUCTION

In recent times epoxy-based structural film adhesives and composite prepreps have been increasingly used, especially in aerospace applications. These materials incorporate a latent curing agent and need only heat to initiate cure. At temperatures well below the cure temperature reactions occur slowly which eventually render the material unusable. Thus, their one part nature, while offering various advantages, results in materials of limited shelf life (commonly 6 months at -18°C). Factors affecting the shelf life, and the performance of the material when cured, are of considerable practical importance. Although a large amount of work has been undertaken on moisture effects in cured epoxy systems, the effects on uncured material have been neglected.^{1,2}

In a study of the room-temperature ageing of a structural adhesive containing triglycidyl(4-aminophenol) (TGAP) it was found that the hydrolytic stability of this compound was poor.³ This epoxy resin is being used increasingly in adhesives and composites for high temperature applications and so its hydrolytic stability has been further examined, together with that of tetraglycidyl(methylene-dianiline), an epoxy resin also extensively used in aircraft composites. In addition, a number of model compounds have been studied in an attempt to establish some of the factors determining the susceptibility to hydrolysis. The effect of this moisture sensitivity on the performance of a structural adhesive described earlier³ has also been investigated.

* Presented at the 12th Annual Australian Polymer Symposium, Blackheath, New South Wales, Australia, May 1981.

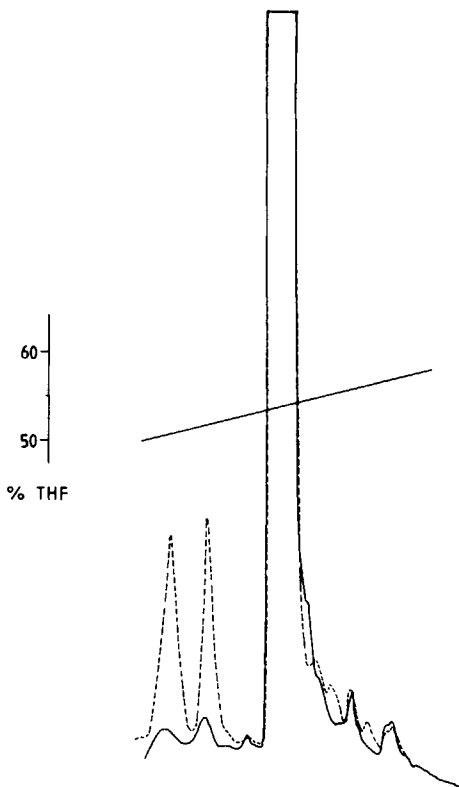


Fig. 1. HPLC analysis of triglycidyl(4-aminophenol) (A grade). (—) Initially; (---) after 3 days at 60°C, 96% relative humidity.

EXPERIMENTAL

Three commercially available epoxy resins were obtained from Ciba-Geigy Australia Ltd. These were tetraglycidyl(methylene-dianiline) (MY 720) and two grades of triglycidyl(4-aminophenol), designated ERL 0500 and ERL 0510, the latter being a more pure form.

A sample of the reactive diluent, phenyl glycidyl ether, was obtained from Koch-Light Laboratories Ltd.

The structural adhesive was a commercial, 177°C curing, film adhesive which contained about 33% by weight overall of ERL 0500, 30% of a cresol novolac epoxy resin and 11% of a high-molecular-weight diglycidyl ether of bisphenol-A. The curing agent was dicyandiamide.³ This adhesive is certified for use in aircraft honeycomb construction for high-temperature applications.

Three model compounds of similar structure were prepared as follows.

The method of Everett and Ross⁴ was used to prepare *N,N*-diglycidyl-4-anisidine from 4-anisidine and epichlorohydrin by way of the chlorohydrin intermediate *N,N*-bis(2-hydroxy-3-chloropropyl)-4-anisidine. It was found necessary to isolate and purify this intermediate. A product of 90% purity based on epoxide content was obtained in 69% yield from which a purer product (boiling point 146°C/0.2 Torr) was isolated. *N,N*-diglycidylaniline and *N*-glycidyl-*N*-methylaniline were prepared in a similar manner from epichlorohydrin and aniline⁵ or methylaniline⁶ but in neither case was it necessary to isolate the

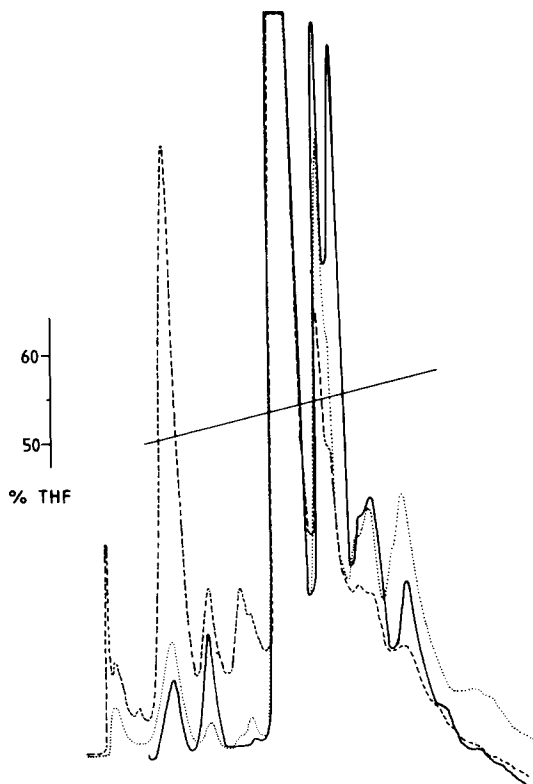


Fig. 2. HPLC analysis of triglycidyl(4-aminophenol) (B grade). (—) Initially; (---) after 2 days at 60°C, 96% relative humidity; (.....) after 10 days at 60°C, dry.

chlorohydrin intermediate. The final products were recovered by vacuum distillation (boiling point 133°C/0.25 Torr in the former case and 95°C/0.5 Torr in the latter).

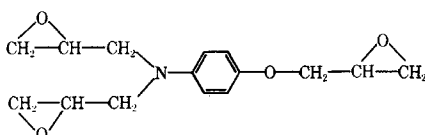
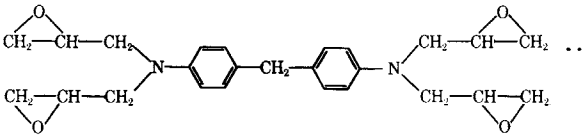
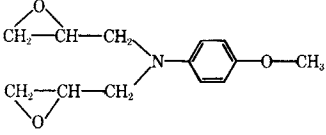
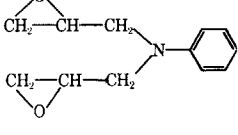
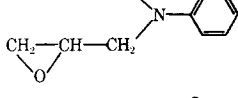
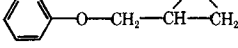
Both crude and purified materials were used in the stability trials in order to assess the effect of purity. A measure of the purity of all epoxy compounds used in this work, based on epoxy content, is shown in Table I. These values were determined by the standard nonaqueous titration method⁷ using chlorobenzene since it is a convenient solvent for extraction of the epoxy resin component from structural adhesives.

Hydrolytic stability was studied by ageing the materials at 60°C and 96% relative humidity; these conditions are designated as hot/wet. For comparison, some samples were stored at 60°C without a special environment and this is termed hot/dry conditions. Samples were removed at intervals and examined by high-pressure liquid chromatography (HPLC), thin-layer chromatography (TLC), infrared (IR) spectroscopy, and chemical analysis for epoxide content.

A modified Varian 8500 instrument with an Altex 153 UV detector set at 254 nm was used for HPLC. The equipment was operated in the reverse phase, gradient elution mode with a DuPont Zorbax CN column and THF/water as the solvent combination.

For TLC, samples were dissolved in acetone and applied as single spots to Merck precoated plates (silica gel GF₂₅₄, 0.25 mm). Components were separated

TABLE I
 Epoxy Compounds Used and Their Purity

Compound	% Purity ^a		
	A Grade	B Grade	
Triglycidyl(4-amino phenol)		97	78
Tetraglycidyl-(methylene-dianiline)		...	86
<i>N,N</i> -diglycidyl-4-anisidine		95	90
<i>N,N</i> -diglycidyl-aniline		97	91
<i>N</i> -glycidyl- <i>N</i> -methylaniline		96	81
Phenyl glycidyl ether		99	...

^a Based on epoxy equivalent weight.

by two successive developments to a height of 15 cm with 1:1 acetone/petroleum spirit (boiling point 40–60°C) in saturated chambers. Plates were scanned at 254 nm parallel to the solvent flow direction with a Zeiss PMQ II single beam UV-vis spectrophotometer in the plate scanning mode.

For IR analysis of components, an acetone solution of the sample was spotted across a 20 cm TLC plate which was then chromatographed as described. Bands of components, located under 366 nm light, were removed, separated from silica gel and incorporated into KBr disks. The IR spectra were determined using a Jasco IRG spectrophotometer.

Moisture contents were determined with a Photovolt Aquatest II automatic Karl Fischer titrator.

Samples of adhesive, aged in the hot/wet and hot/dry conditions, were used to make aluminium-aluminium single overlap joints which were tested in tensile-shear at 20 and 177°C. The aluminium was 1.6 mm 2024-T3 Alclad for which the surface preparation was a vapor degrease in 1,1,1-trichloroethane followed by a chromic acid etch. Joints were made in a heated platten press using the recommended cure cycle for the adhesive (1 hr at 177°C and 0.33 MPa). Joint geometry and test methods were in accord with standard procedures.⁸

RESULTS AND DISCUSSION

Chromatographic Studies

HPLC analysis of the two grades of triglycidyl(4-aminophenol) stored for a few days at 60°C and 96% relative humidity are compared with untreated material in Figures 1 and 2. Initially, the principal difference between the two grades was that the purer form contained no higher-molecular-weight oligomers and less of other minor impurities. In each case the effect of exposure to the hot/wet atmosphere was the progressive appearance of (or increase in) a number of peaks corresponding to compounds increasingly more polar than the parent epoxy compound and a reduction in the size of the peaks attributable to the oligomers. Changes in the peak height of the parent, monomeric compound were not determined from these experiments due to detector overload. The samples suddenly became solid, and insoluble in THF, after about 3.5 and 2.5 days, respectively, for the A and B grades.

A similar pattern was indicated by TLC (Fig. 3). In all cases, the assignment of peaks into the broad categories of oligomers or hydrolysis products has been made on the basis of IR spectra and chromatographic behavior. However, it has not been possible to identify precisely the compounds responsible for the observed peaks. The three major peaks closest to the monomer peak are due to oligomers while most of the rest arise from hydrolysis products. As indicated

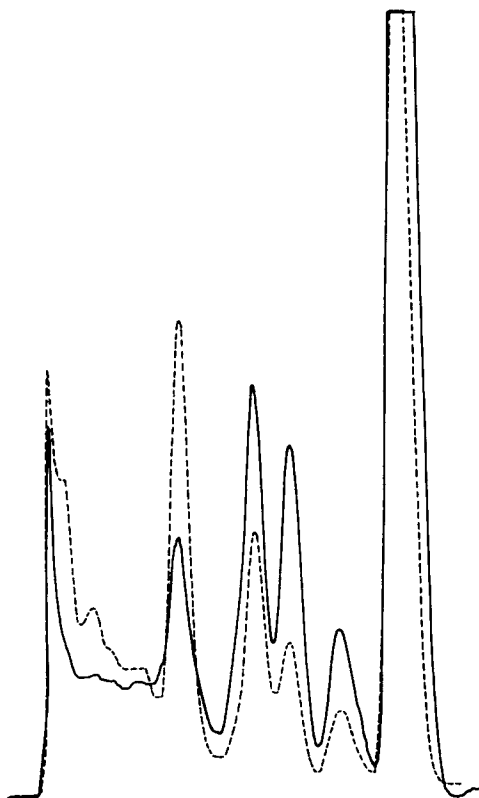


Fig. 3. TLC analysis of triglycidyl(4-aminophenol) (B grade). (—) 5 hr at 60°C, 96% relative humidity; (---) 45 hr at 60°C, 96% relative humidity.

by HPLC, the peak heights due to oligomers decreased and those due to hydrolysis products increased during two days in the hot/wet atmosphere. A decrease in the monomer peak is also visible in this case.

These materials were also studied under hot/dry conditions. The same set of additional peaks as before was observed but the relative peak heights differed and the time for the changes was greatly increased (Fig. 2). For example, the B grade material took about 10 days to solidify (cf. 2.5 days in the wet conditions).

Changes occurring in the HPLC analysis of tetraglycidyl(methylene-dianiline) stored in the hot/wet conditions are shown in Figure 4. This material became solid after about 8.5 days. Under hot/dry conditions the pattern of peaks was again similar (Fig. 4) but the time to solidification increased to about 38 days.

For the two grades of diglycidylaniline in the hot/wet conditions an induction period of about 7 days occurred after which additional, hydrolysis peaks began to appear on the polar side of the monomer peak in the HPLC analyses. This pattern was reflected in the change in epoxide content. The A and B grades became solid after 40 and 33 days, respectively.

Detailed HPLC studies were not undertaken on the other model compounds.

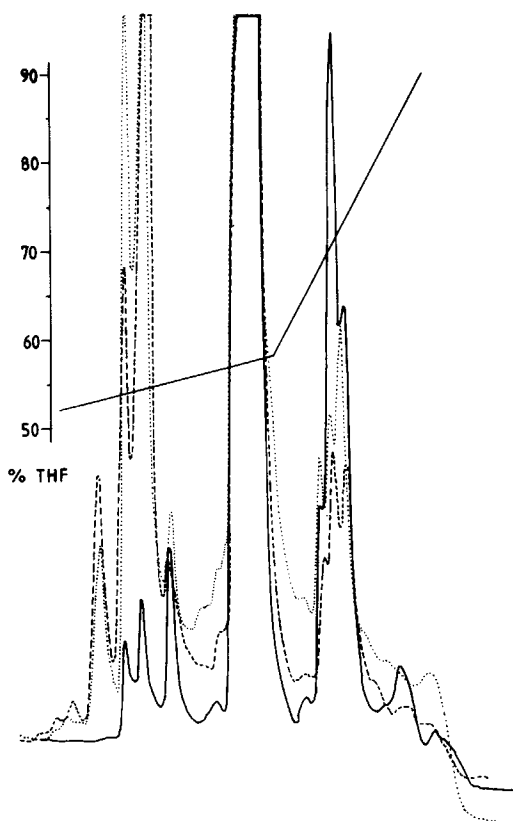


Fig. 4. HPLC analysis of tetraglycidyl(methylene-dianiline) (—) initially; (---) after 8 days at 60°C, 96% relative humidity; (.....) after 30 days at 60°C, dry.

Changes in Epoxide Content

The rate of change of epoxide content was also determined as a means of comparing the various systems. In most cases the pattern was a period of slow decrease in epoxide content followed by a rapid change and solidification of the material (Fig. 5). The rate of epoxide loss varied between duplicate runs but in each instance the B grade material reacted more rapidly than the purer form. However, phenyl glycidyl ether was unaltered after 130 days.

So as to rank the various compounds in an order of sensitivity to moisture, the time to a 20% reduction in epoxide content was arbitrarily taken as a reference point. These values are shown in Table II. A similar series of experiments was performed on a structural adhesive to observe the effect of moisture on a fully formulated composition. These results are included in Figure 5 and Table II. Some comparative data for material stored under hot/dry conditions are also shown. The dry state cannot be regarded as anhydrous as the materials themselves contain small amounts of moisture. The adhesive, for example, contained about 0.5% water by weight.

Reduction of the epoxide content by hydrolysis would result in impaired performance of the cured material, especially at high temperature, because of

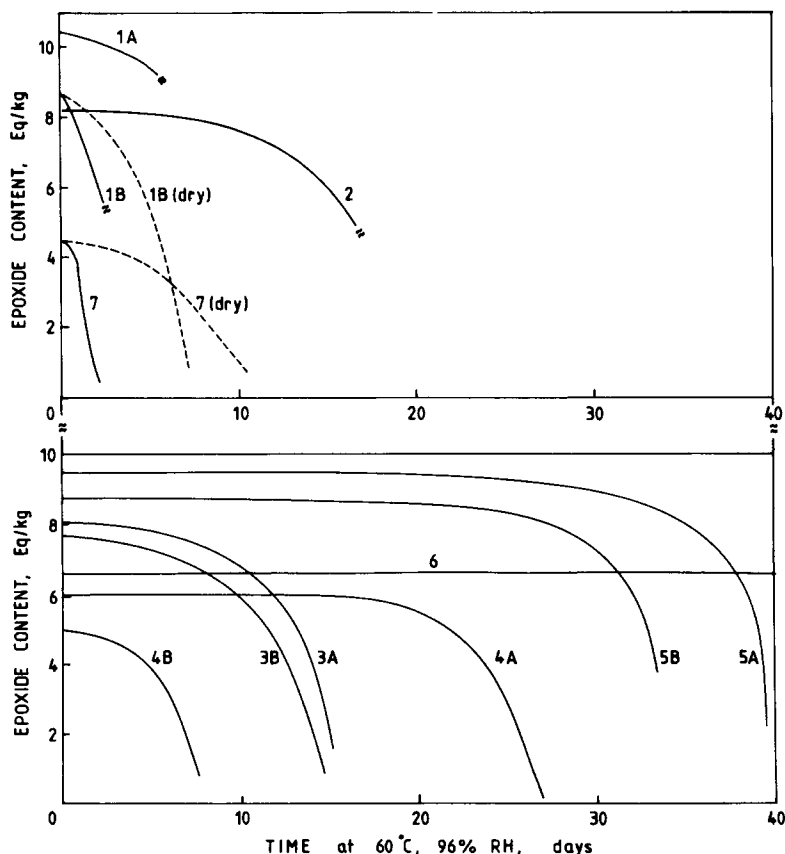


Fig. 5. Rate of loss of epoxide content. Top, commercial systems; bottom, model compounds. (1) TGAP; (2) MY 720; (3) diglycidyl 4-anisidine; (4) methyl glycidyl aniline; (5) diglycidyl aniline; (6) phenyl glycidyl ether; (7) structural adhesive.

TABLE II
Time to 20% Loss in Epoxide Content Under 60°C, 96% Relative Humidity Conditions

System	Time (days)	
	A Grade	B Grade
Triglycidyl(4-aminophenol)	ca. 4.5	ca. 1.7 (3.3) ^a
Tetraglycidyl(methylene-dianiline)	...	ca. 14
<i>N,N</i> -diglycidyl-4-anisidine	10	9
<i>N</i> -glycidyl- <i>N</i> -methylaniline	23.7	4.5
<i>N,N</i> -diglycidylaniline	36.1	30.2
Phenyl glycidyl ether	>>130 ^b	...
Structural adhesive	...	1.2 (5.6) ^a

^a Values for 60°C, dry.

^b No change after 130 days.

the modified crosslink density and thus lower T_g .⁹ This aspect was examined by measurement of the tensile-shear strength of single overlap joints made with adhesive aged under hot/wet conditions (Fig. 6), and it is evident that the high-temperature strength of the joints was halved after less than 24 hr ageing. Joints made with adhesive aged for the same time under hot/dry conditions showed no loss of strength.

Examination of these results indicates that *N*-glycidyl aromatic amines are sensitive to moisture, especially when the compound is substituted in the 4 position. Under the same conditions glycidyl ether-type epoxides, represented in this work by phenyl glycidyl ether, are resistant to moisture (Table II). This is in accord with the proven high stability of the common diglycidyl ether of bisphenol-A (DGEBA) epoxy resins.

The need for storage and handling procedures to minimise moisture absorption by structural adhesives and composite prepregs which are based on *N*-glycidyl aromatic amine resins is clearly evident. Adequate protection from water condensed during thawing of material removed from a freezer is required.

It appears that the initial hydrolysis is followed by a self-curing reaction which accelerates the rate of epoxide loss and leads to the formation of a solid material

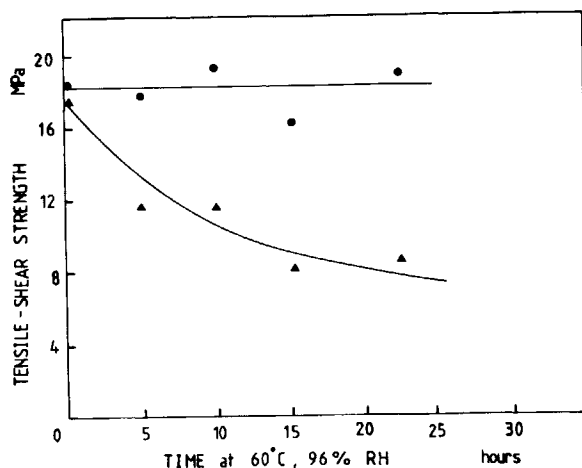


Fig. 6. Tensile-shear strength of single lap joints using adhesive aged at 60°C, 96% relative humidity. Test temperature (●) 20°C; (▲) 177°C.

of low softening point. The large number of compounds detected by chromatography indicates that a complex series of reactions occurs. Reactions of epoxide with hydroxyl-containing compounds under acidic or basic conditions can yield primary or secondary alcohols and also polyethers from the further reaction of epoxide with alcohols.¹⁰ Without a catalyst high temperatures are usually required: the products depend on the experimental conditions^{10,11} and several mechanisms have been proposed to account for the observations.¹⁰ In the present case the epoxy resins are themselves tertiary amines which, in the presence of water, could act as catalysts for epoxide homopolymerization.¹²⁻¹⁴ A wide range of polar products, together with a reduction in the epoxide content, is thus not unexpected in the present work.

A detailed kinetic study of the epoxy structure-rate relationships has not been attempted because of the pronounced dependence of the rate on the purity of the epoxy compound. Some of the impurities in these epoxy materials evidently affect the rate of reaction significantly. Small amounts of phenols and compounds that contain chlorine, known modifiers of epoxy cure reactions,¹⁰ are likely impurities during the manufacture of these epoxy materials. A lack of detailed knowledge of the identity of the impurities has precluded closer examination at present.

Commercial epoxy resins may be of variable purity within the one grade. This arises from such factors as batch-to-batch variations in resin production and the introduction of impurities, of various types and amounts, from the use of precursors from different sources. The present work indicates the need for close control of the purity of *N*-glycidyl aromatic amine resins for use in critical applications. However, epoxy content is not an adequate measure of resin purity for this purpose since it takes no account of the nature of the impurities. Chromatography is a better indicator of resin quality.

The advantages of using high purity resins, which are less moisture sensitive, are also indicated. A comparative study of two adhesives, based on the two grades of TGAP, is in progress under ambient temperature conditions. There are preliminary indications that the greater stability of the purer grade is reflected in a longer shelf life of the adhesive.

CONCLUSIONS

Epoxy resins based on *N*-glycidyl aromatic amines are sensitive to moisture, especially when the compound is 4 substituted. The initial hydrolysis is followed by homopolymerization such that losses of 20% of epoxide content can occur in a few days at 60°C and 96% relative humidity. The rate of reaction is strongly influenced by impurities in the resin. Under the same conditions ether-based epoxy compounds are resistant to moisture.

A number of commercial film adhesives and composite prepregs extensively used in aerospace applications contain the *N*-glycidyl aromatic amine moiety and are thus moisture sensitive.

The importance of maintaining these materials in a dry condition before cure is clearly evident and the value of using high purity epoxy compounds in formulations for aerospace applications is also demonstrated.

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Received September 22, 1980

Accepted January 19, 1981