

# Aging and Performance of Structural Film Adhesives.

## I. A Comparison of Two High-Temperature Curing, Epoxy-Based Systems

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### Synopsis

The room temperature aging of two epoxy adhesives, both of which are cured at 177°C and contain the moisture sensitive resin triglycidyl(4-aminophenol), has been examined. It has been found that hydrolysis of this resin is the major cause of reduction in epoxide content during aging. This in turn is largely responsible for the deterioration in the performance, especially at high temperatures, of bonded joints made with aged adhesive. The advantages of using high purity resins in adhesive formulations have been demonstrated.

### INTRODUCTION

The use of adhesive bonding for structural applications in aircraft is now well established. Many adhesives for these applications are in the form of one part films of very limited shelf life even at low temperatures. The increasing use of bonding in critical areas, including primary aircraft structure, has placed additional emphasis on quality control of uncured adhesives, on chemical means of assessing the extent of reaction which has occurred during storage, and on the effect of any such reaction on the performance of the cured material.

In a recent publication,<sup>1</sup> preliminary results on the ambient aging of an epoxy-based, 177°C-curing, structural film adhesive were reported. This work related principally to changes in the chemical properties of the adhesive as indicated by molecular weight distribution, solubility, and epoxide content. This study has now been extended to include results of mechanical testing of aluminum-aluminum joints made with aged adhesive as well as further examination of chemical aspects of aging.

The aging of another, similar, 177°C-curing film adhesive has also been studied. The principal epoxy resin, common to both these adhesive formulations but of different grades, is an *N*-glycidyl aromatic amine type recently shown<sup>2</sup> to be moisture-sensitive and strongly influenced by impurities in the resin. The effect of this on the aging of adhesives has been examined by a comparison of the performance of these two adhesives.

### EXPERIMENTAL

The two adhesives used in this work are designated A and B. Both are designed for bonding honeycomb-to-metal and metal-to-metal in aerospace applications for service up to about 200°C. The recommended cure cycle is 1 h

at 177°C and 350 kPa (Adhesive A) and 1 h at 175°C and 150–700 kPa (Adhesive B). The nominal weight is 0.44 kg/m<sup>2</sup> (A) and 0.38 kg/m<sup>2</sup> (B). Their respective performance as adhesives is indicated in Figure 1 using tensile-shear results taken from the manufacturers' data sheets. No information is supplied on chemical composition.

The manufacturer of Adhesive A recommends storage at -18°C "to obtain maximum shelf life" (unspecified). For Adhesive B a shelf life of 12 months at 0°C is quoted. Since both materials are imported into Australia, their precise thermal histories are unknown, but at the commencement of this work both were several months old and the performance of each was close to the manufacturers' data.

For aging, about 30 cm square pieces of the adhesives were stored in polyethylene bags at room temperature (around 23°C). Samples were removed at intervals for testing or, if necessary, stored at -18°C until required.

The overall composition of Adhesive A was previously determined.<sup>1</sup> Qualitative analysis of Adhesive B was achieved by a combination of thin layer chromatography (TLC) and infrared spectroscopy (IR).

The acetone soluble material was separated on silica gel TLC plates (Merck; silica gel GF<sub>254</sub>, 0.25 mm); several mixtures of petroleum spirit (40–60°C) and acetone were used to achieve satisfactory separation of the components. Semipreparative scale TLC yielded sufficient of each component for IR identification using a Jasco IR-G double beam spectrophotometer. The acetone insoluble portion was extracted with dimethylformamide and the single component thus isolated identified by IR.

Quantitative analysis was accomplished by direct scanning of TLC plates using a Zeiss PMQ II spectrophotometer with scanning attachment in the reflective mode. The epoxy resins Shell Epon 828 (diglycidyl ether of bisphenol A),

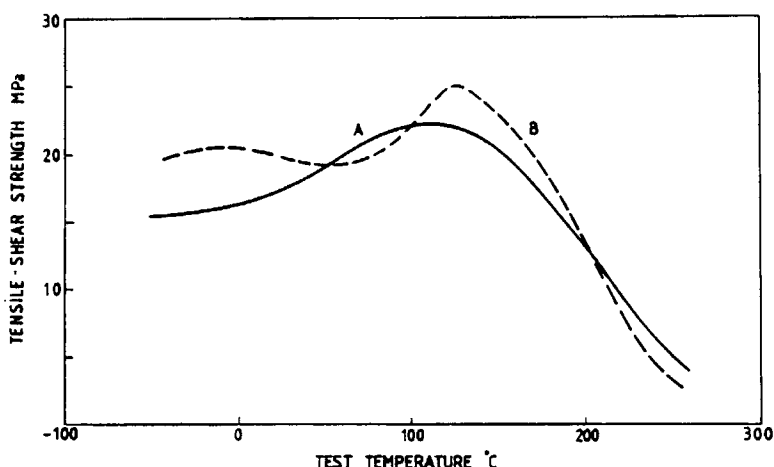


Fig. 1. Performance comparison of the two adhesives taken from manufacturers data sheets. Al-Al single overlap joints primed with the recommended primer. A tested according to MMM-A-132<sup>3</sup>; B according to DTD 5577.<sup>4</sup>

Ciba-Geigy ERL 0510 [triglycidyl(4-aminophenol)], and Shell Epon 1031 (tetraglycidyl ether of tetraphenolethane) were used as standards.

For high pressure liquid chromatography (HPLC) a modified Varian 8500 instrument with an Altex 153 UV detector set at 254 nm was used. The equipment was operated in the reverse phase, gradient elution mode with a DuPont Zorbax CN column and a combination of tetrahydrofuran (THF) and water (flow rate 1.0 mL/min) as the solvent.

Material responsible for a number of peaks in the HPLC traces was collected for identification by IR, several passes usually being required to accumulate sufficient material. These components were analyzed with a Perkin-Elmer 580B ratio recording double beam spectrophotometer interfaced with a Model 3500 data handling system. The HPLC solvent was allowed to evaporate in a current of air; the residue was dissolved in 20–30  $\mu$ L of THF or dichloromethane and was applied to an area approximately 10 mm  $\times$  3 mm on a KBr window. The window was placed at the IR beam focus and adjusted to give maximum absorption at a region of high absorption (usually 1510  $\text{cm}^{-1}$ ).

Spectra were recorded at a spectral slit width of 3–4  $\text{cm}^{-1}$  (mode 4) with data collection at 1  $\text{cm}^{-1}$  intervals over the range 4000–400  $\text{cm}^{-1}$ . Sample spectra were corrected for "blank" absorption of the KBr window by digital subtraction and the result smoothed (Savitsky-Golay, 13 point) and digitally expanded in absorbance to give a spectrum in which the strongest band was between 0.8 and 1.0 absorbance units. Selected areas of the spectrum were expanded further as required. The strongest bands in the original spectra ranged between 0.03 and 0.3 absorbance units.

Epoxide content was determined by titration as previously described.<sup>2</sup> Moisture content was measured with a Photovolt Aquatest II Automatic Karl Fischer titrator.

Single overlap joints were made with 1.6 mm 2024-T3 Alclad aluminum sheet for which the surface preparation was a vapour degrease with 1,1,1-trichloroethane followed by a chromic acid etch. No primer was used. Joints were made in a heated platen press using the cure cycle recommended for the adhesive. Joint geometry and test methods were in accord with standard procedures.<sup>3</sup> The testing was accomplished with a model TT-C-L Instron tensile testing machine.

Flow of the adhesive was assessed by curing a 38-mm square piece of adhesive between Teflon-coated sheets in the press as above and calculating the flow from the increase in area.

The effects of adhesive aging on joint durability were assessed in certain cases using single overlap joints made with adhesive aged at room temperature for various lengths of time. The bonded panels were cut into 25 mm wide strips and immersed in water at 40°C for 1000 h. Specimens were then dried and tested.

Dynamic mechanical properties of cured adhesive specimens were assessed with a Rheovibron DDV-II-C direct reading dynamic viscoelastometer. Samples for examination were cured in batches in the press, using a polyester film template, to ensure equivalent thermal history. The cure cycle was that recommended by the manufacturer. The equipment was operated in the tensile mode at a frequency of 110 Hz with a heating rate of about 2°C/min.

TABLE I  
Overall Composition of Adhesive A

Component	Amount (wt %)
Triglycidyl(4-amino phenol) <sup>a</sup>	33
Cresol novolac epoxy resin	30
Diglycidyl ether of bisphenol A <sup>b</sup>	11
Dicyandiamide	8
Asbestos	8
Woven glass support	10

<sup>a</sup> Impure grade, e.g., ERL 0500.

<sup>b</sup> Higher molecular weight than, e.g., Epon 1009.

## RESULTS AND DISCUSSION

### Chemical Studies

The composition of the two adhesives was determined, by a combination of chromatographic techniques and infrared analysis, as that given in Tables I and II and Figure 2. The principal epoxy resin in each case is based on triglycidyl(4-aminophenol). Examination by HPLC shows, as detailed below, that Adhesive A contains an impure grade of this epoxy resin, such as Ciba Geigy's ERL 0500, in that it includes significant amounts of oligomers and unidentified impurities, while Adhesive B is based on a purer form of the resin (ERL 0510 for example) containing virtually no higher oligomers and lower levels of impurities. Infrared analysis showed that both adhesives contain dicyandiamide (dicy) as the curing agent and that substantial amounts of a poly(ether sulphone) are incorporated in Adhesive B.

The overall epoxide content of each adhesive was measured at intervals during the room temperature aging and the results are shown in Figure 3. Adhesive A changes slowly almost from the beginning of this trial, with a more rapid reduction in epoxide content after about 26 weeks, whereas Adhesive B appears to be essentially unaltered for the first 20 weeks. Similarly, the overall solubility in such solvents as acetone and toluene follows the same pattern of a slow reduction for Adhesive A over about 20 weeks and then a more rapid drop whereas Adhesive B alters little for more than 30 weeks.

TABLE II  
Overall Composition of Adhesive B

Component	Amount (wt %)
Triglycidyl(4-amino phenol) <sup>a</sup>	33
Diglycidyl ether of bisphenol A <sup>b</sup>	5
Tetraglycidyl ether of tetraphenolethane <sup>c</sup>	7
Poly(ether sulphone) <sup>d</sup>	25
Dicyandiamide	4
Aluminum powder	22
Woven nylon 66 support	4

<sup>a</sup> Pure grade, e.g., ERL 0510.

<sup>b</sup> Low molecular weight, e.g., Epon 828.

<sup>c</sup> For example, Epon 1031.

<sup>d</sup> Not P1700 of Union Carbide.

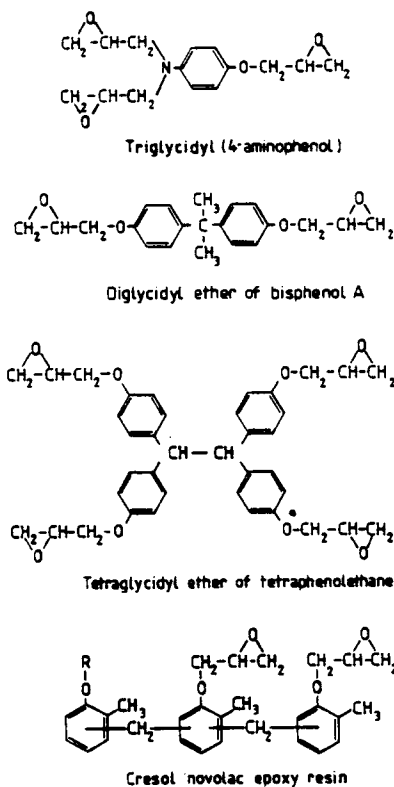


Fig. 2. Structural formulas of epoxy resins.

Broadly the change in epoxide content and solubility of Adhesive A is the same as that previously reported,<sup>1</sup> but the rate of change is considerably slower in the present investigation. Significant batch-to-batch variations were demonstrated in the previous work, and the present study involved yet another batch of adhesive, and also the weave of the glass support was different.

The temperature at which the aging occurs (about 23°C) is far below the cure temperature of these systems (about 175°C) and well below the temperatures

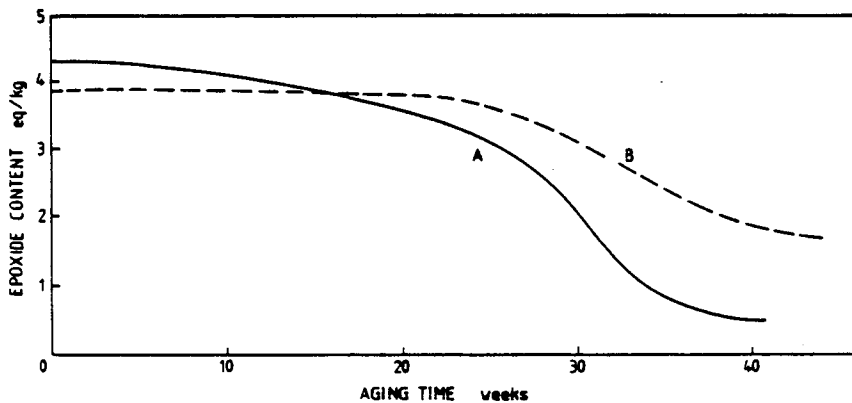


Fig. 3. Change in epoxide content with time.

at which dicy dissolves in epoxy resins (70–80°C). The dicy content of aged samples of Adhesive A was determined by IR, and it was found that the values decreased gradually from the initial 7.5% by weight to around 7.2% over 36 weeks aging. Since the epoxide content of Adhesive A decreased by about 80% and its solubility in toluene decreased by 75% in that time, it is clear that the changes during aging cannot be regarded as the normal cure reaction proceeding slowly but rather are indications of other, side reactions.

HPLC analysis of aged samples of the two adhesives was undertaken and examples, using identical experimental conditions, are shown in Figures 4 and 5. The extinction coefficient of the triglycidyl(4-aminophenol) is so much larger at 254 nm than that of any of the other components that the early segment of the chromatogram is in each case completely dominated by the peaks due to this compound and its oligomers and derivatives. The difference in higher oligomer content in the two adhesives is clearly evident from the height of the peaks eluting immediately after the parent epoxy peak (elution volume 9–10 mL). In Adhesive B the peaks eluting the region 10–15 mL were shown by IR analysis to be due principally to tetraglycidyl ether of tetraphenolethane oligomers while those

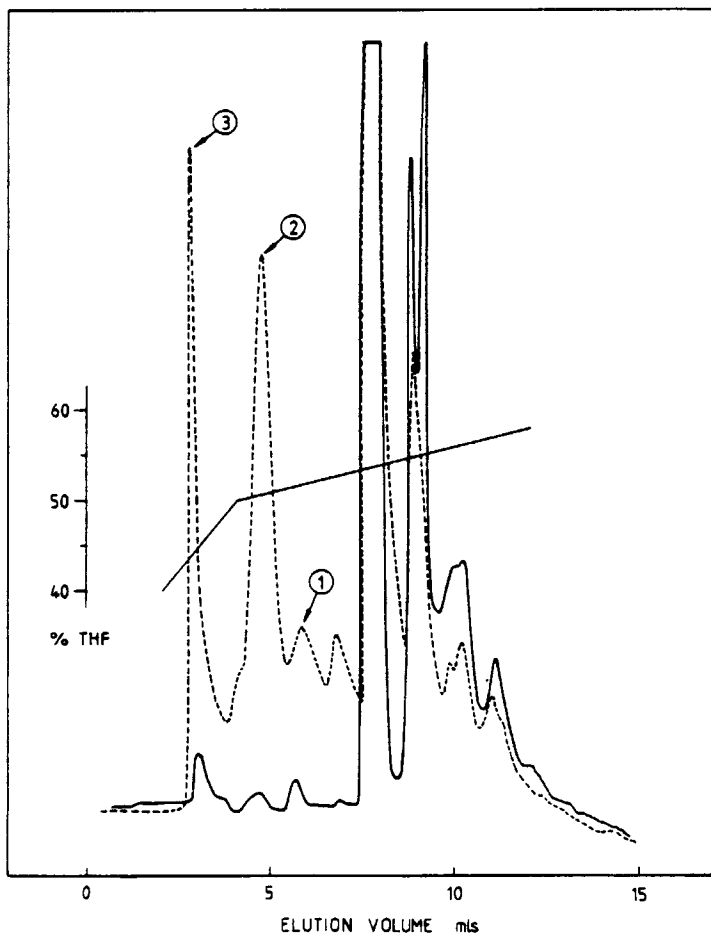


Fig. 4. HPLC analysis of Adhesive A. (—) Initial material; (---) aged 36 weeks.

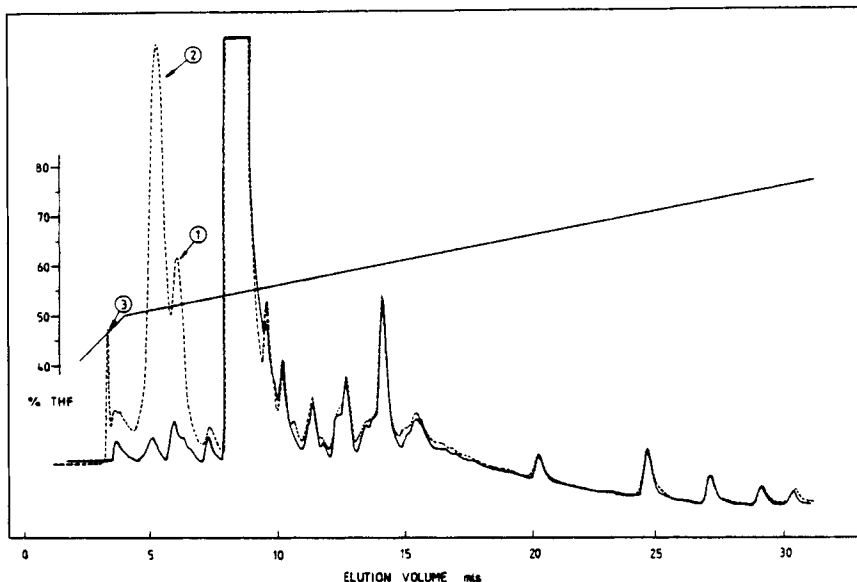


Fig. 5. HPLC analysis of Adhesive B. (—) Initial material; (---) aged 36 weeks.

eluting at longer volumes are a combination of high molecular weight DGEBA oligomers and some poly(ether sulphone).

On aging, additional peaks, more polar than the parent triglycidyl(4-aminophenol) compound, are observed in the two adhesives, at the same elution volumes, and this is in agreement with previous results on the accelerated aging of this epoxy resin.<sup>2</sup> The rate of increase in height of the additional peaks is considerably greater in the case of Adhesive A than in that of Adhesive B (the rates for the two most obviously changing peaks, designated 2 and 3 in the HPLC analyses, are shown in Figure 6), and this is in accord with the previous finding of greater stability being displayed by the purer epoxy resin.<sup>2</sup> In Adhesive A the proportions of the two triglycidyl(4-aminophenol) oligomers eluting immediately after the parent epoxy (elution volume 9–10 mL) change substantially during aging. This aspect is under further study.

It has been shown<sup>2</sup> that *N*-glycidyl aromatic amine-type epoxy resins are moisture sensitive and that impurities in the resin can significantly accelerate the rate of epoxide loss. Under the same conditions glycidyl ether-type epoxy resins are stable. In an effort to elucidate further these moisture-induced changes, fractions corresponding to the peaks designated 1, 2, and 3 in Figures 4 and 5 were collected from HPLC analyses and examined by IR. Corresponding fractions collected from chromatograms of triglycidyl(4-aminophenol) (ERL 0510), which had been boiled for various times in water, were also examined for comparison. The elution volume of peak 3 was essentially that of the free volume of the instrument from injector to detector, that is, this material did not interact with the column packing. IR spectra indicated that all these compounds were of the same type. In comparing spectra of triglycidyl(4-aminophenol) and of the components eluting at volumes corresponding to peaks 1, 2, and 3, particular features which were observed to change were bands near  $3000\text{ cm}^{-1}$  and  $910\text{ cm}^{-1}$  (due to methylene CH stretch in the epoxide ring and epoxide ring breathing

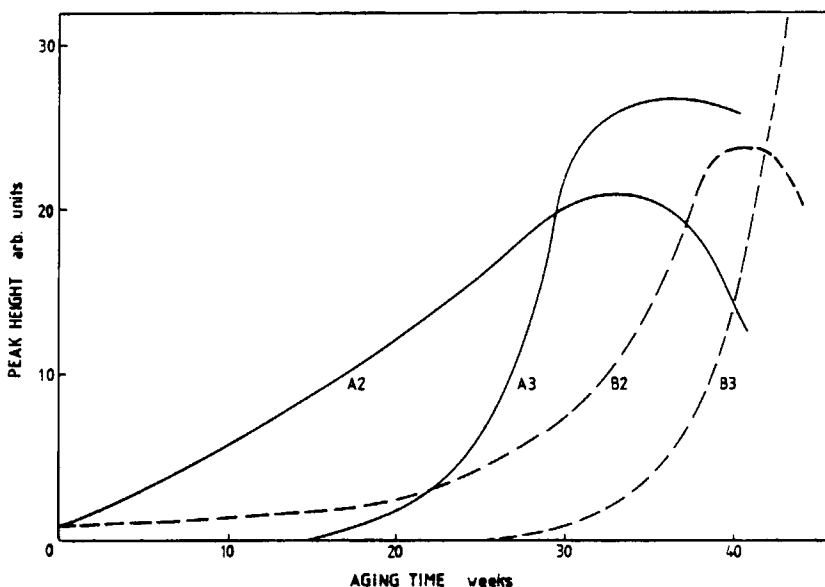


Fig. 6. Change in selected HPLC peaks. A2 and A3, see Figure 4; B2 and B3, see Figure 5.

vibrations respectively), hydroxyl OH stretch near  $3400\text{ cm}^{-1}$ , and bands near  $1130\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  (due to C—O stretch in secondary and primary alcohols). The epoxide absorptions in triglycidyl(4-aminophenol) and peaks 1, 2, and 3 decreased roughly in the proportions 3:2:1:0 while the hydroxyl absorption increased approximately in the reverse proportion. Infrared spectra of corresponding fractions from the two adhesives were not significantly different. Representative spectra are shown in Figure 7.

Peak 3 also contained dicy, although its contribution to the spectrum was somewhat modified from that of dicy alone. The IR spectrum of a mixture of dicy and fully hydrolyzed triglycidyl(4-aminophenol) was the same as that of peak 3. It was thus concluded that peak 3 consists of a mixture of dicy and a hydrolysis product rather than a reaction product of the epoxy resin and dicy.

A more rigorous analysis has not been attempted because of the small amounts of material available and a lack of knowledge of the extent of conformity to Beer's Law and of the effect of changes in polarity arising from the increased hydroxyl content. However, from the chromatographic and IR data it seems probable that peaks 1, 2, and 3 are due to the hydrolysis products of triglycidyl(4-aminophenol), that is, material having 1, 2, or 3, respectively, epoxide groups hydrolyzed (the latter also containing some dicy).

It was also shown previously that the loss of epoxide content was "autocatalytic," in that the initial hydrolysis products assist the subsequent homopolymerization.<sup>2</sup> The three glycidyl ether-type epoxy compounds in these adhesives (cresol novolac, DGEBA, and tetraglycidyl ether of tetraphenolethane), although substantially more resistant to hydrolysis than *N*-glycidyl aromatic amines,<sup>2</sup> could be expected to participate in the subsequent polymerization giving an enhanced rate of reduction of epoxide content. This may contribute to the difference in the rate of loss of epoxide observed in the two adhesives (Fig. 3). The rate and extent of moisture uptake would also be important. The moisture



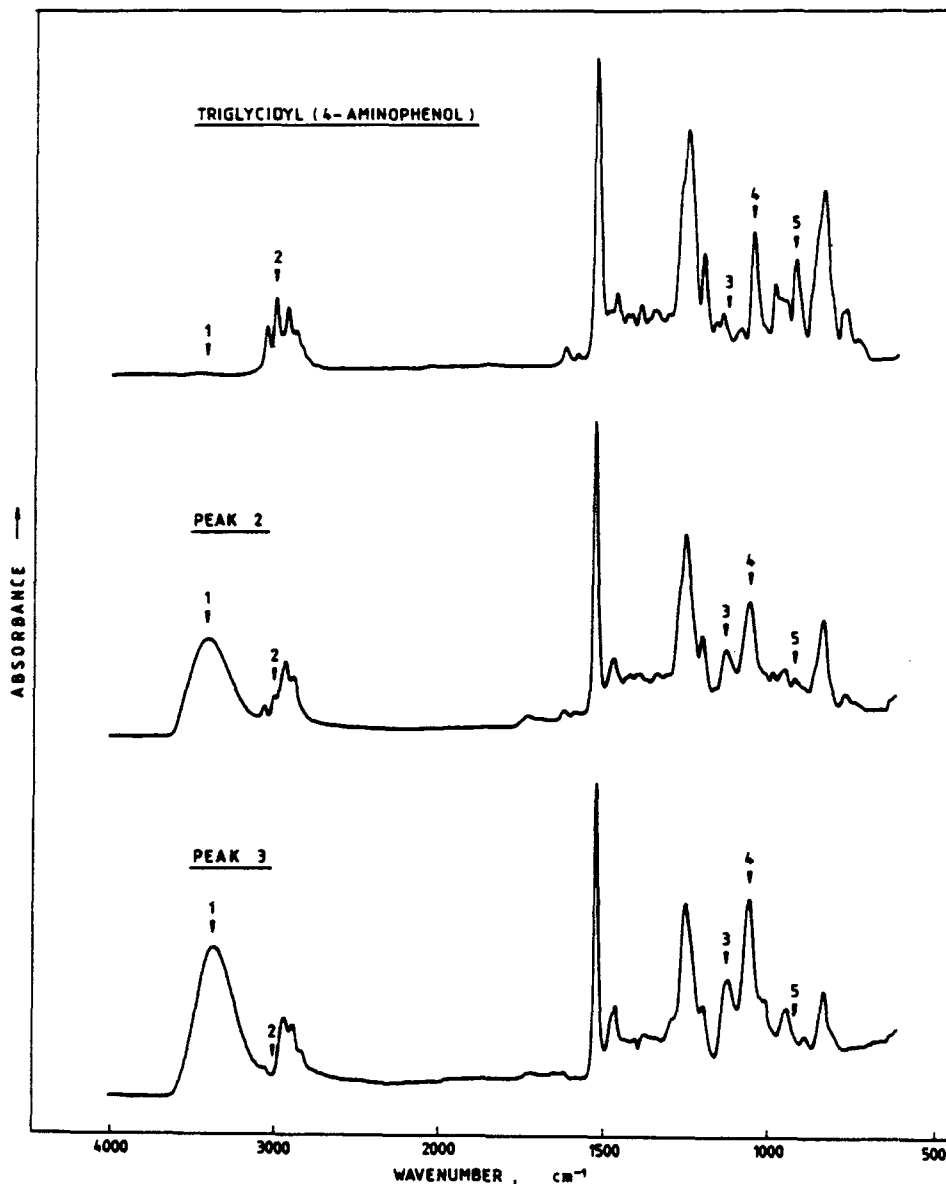


Fig. 7. IR spectra of HPLC fractions from Adhesives A and B. Indicated bands are due to: (1) O—H stretch; (2) C—H stretch in epoxy ring; (3) C—OH stretch in secondary alcohol; (4) C—OH stretch in primary alcohol + C—O—C in ether; (5) epoxy ring breathing vibration.

content of Adhesive A was found to change from 0.66% by weight for the unaged material to 0.76% after 10 weeks aging and 0.96% after 20 weeks. Similar values for moisture uptake have been reported for other adhesives.<sup>5</sup>

A gradual loss of epoxide was reported during the room temperature aging at low humidity of an adhesive based on tetraglycidyl(methylenedianiline).<sup>6</sup> In that case the IR absorbance at  $910\text{ cm}^{-1}$  decreased linearly by about 50% over 8 weeks aging. The change was attributed to homopolymerization, but, in view of this resin's moisture sensitivity<sup>2</sup> and the effects of aging on the high temper-

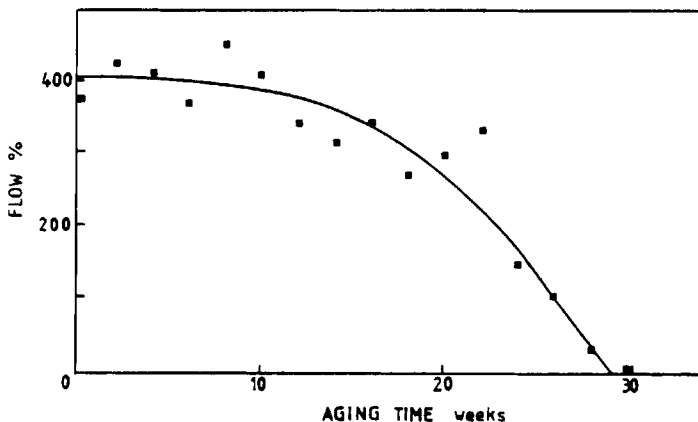


Fig. 8. Change in % flow with aging time for Adhesive A.

ature properties of the cured material, considered below, gradual hydrolysis of the *N*-glycidyl groups seems a more probable explanation.

### Studies on Physical and Mechanical Properties

Changes in the flow behavior of Adhesive A are shown in Figure 8. Obviously, after about 16 weeks aging the extent of polymerization results in a marked reduction in the flow of the adhesive when it is heated.

The tensile-shear strength of single Al-Al lap joints, tested at three temperatures, is indicated in Figure 9. The increased strength observed after some time in the 132°C and ambient cases is attributable to increased flexibility (lower

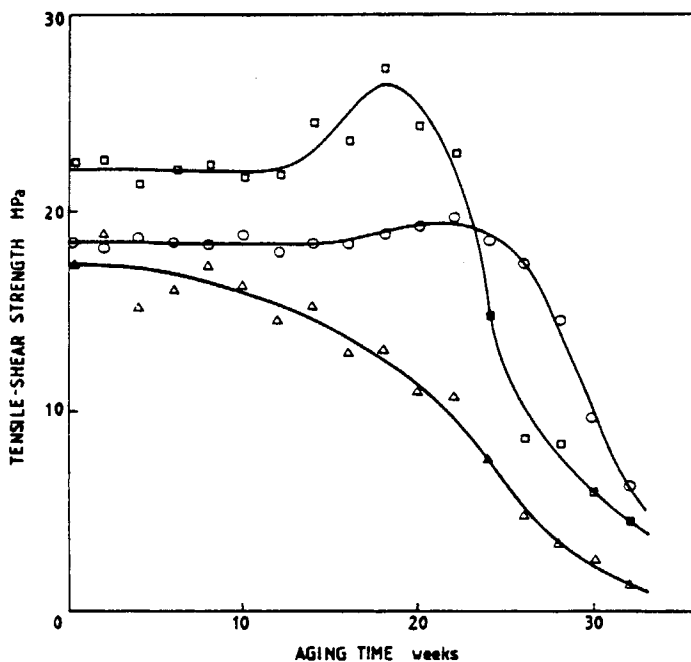


Fig. 9. Tensile-shear strength of Al-Al single overlap joints made with Adhesive A aged for various times. Test temperature: (○) ambient; (□) 132°C; (△) 177°C.

crosslink density) of the adhesive. The reduction in tensile-shear strength at longer times is attributable to reduced flow arising from the advancing homopolymerization, which leads to substrate wetting problems. The decreased crosslink density, resulting from the decreased epoxide content, and thus lower  $T_g$  (see below), largely determines the change in high-temperature performance.

At the completion of this trial, further joints of Adhesive A were made with the original material and tested at ambient and 177°C. It was found that joints of adhesive which had spent the whole of the intervening 19 months at -18°C agreed closely with the initial results. Those made with adhesive which had been subjected to a number of freeze-thaw cycles had reduced high-temperature performance (11.5 MPa compared with 17.8 MPa originally), even though the total time at room temperature was at most a couple of days. Joints tested at ambient temperature showed no effect of adhesive thermal history. Clearly, freeze-thaw cycling has additional, deleterious effects on adhesive performance. This has been noted with other adhesives and has implications for the usefulness of time-temperature integrating devices as age indicators.<sup>7</sup> This matter is being investigated further.

The high-temperature performance is the most sensitive to age-related changes and is the most critical in relation to the service application of these adhesives. Accordingly, the tensile-shear strength of the two adhesives at 177°C was compared (Fig. 10). Once again, Adhesive B displays superior stability to aging.

It has been shown above that during aging a substantial reduction occurs in the epoxide content, initially by hydrolysis of one of the epoxy resins and subsequently by a combination of hydrolysis and polymerization in which all the epoxy resins may take part. When such aged samples are subjected to the normal cure cycle (1 h at 177°C), the resulting polymer network can be expected to differ from that obtained on curing unaged material. The retention of good high-temperature performance in the case of Adhesive B for much longer periods than Adhesive A is attributable in large measure to the greater resistance of the former

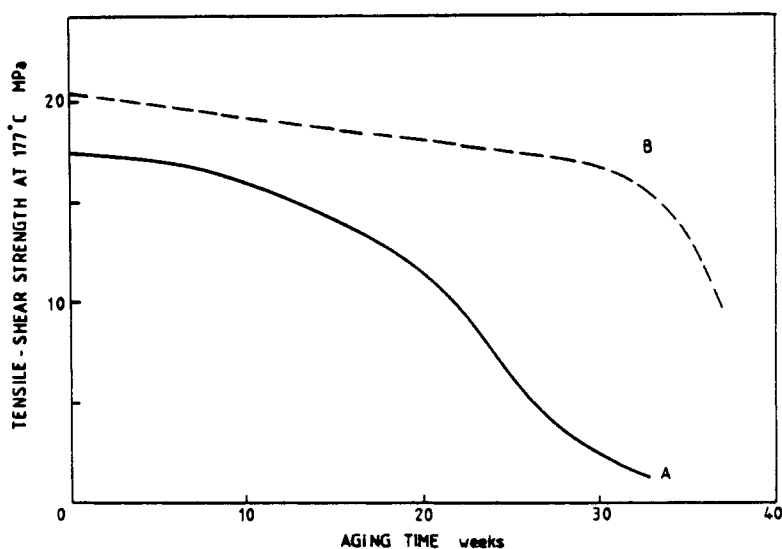


Fig. 10. Change in the high temperature tensile-shear strength with aging.

to hydrolysis, which is a direct consequence of the use of a purer grade of the principal epoxy resin. The presence of the poly(ether sulphone) and aluminum powder may have further moderating influences.

An indication of the differences in the polymer network formed on curing aged samples was gained by examination of the dynamic mechanical proportion of the two adhesives using a Rheovibron. For Adhesive A it was found necessary to have the sample axes at  $45^\circ$  to the glass support weave to minimize contributions from the glass. Such orientation effects were absent from Adhesive B which is on a woven nylon 66 support. Changes in the loss tangent ( $\tan \delta$ ) and the complex modulus up to about  $250^\circ\text{C}$  for a number of aged samples are shown in Figures 11 and 12.

In these measurements the major peak in the  $\tan \delta$  curve occurs at temperatures substantially above the curing temperature ( $177^\circ\text{C}$ ). This points to further curing taking place during the slow heating ( $2^\circ\text{C}/\text{min}$ ) in the Rheovibron resulting in the  $T_g$  of the material, measured by this technique, being higher than that of the original "as cured" state.<sup>8,9</sup> The slowness of the heating rate evidently accounts for the lack of evidence of further curing in the modulus curves. Since all samples were subjected to the same thermal program, it is considered that differences discernible between aged samples are a valid reflection of differences in the structure of those samples.

For Adhesive A, aging gives rise to substantial modification in the loss tangent

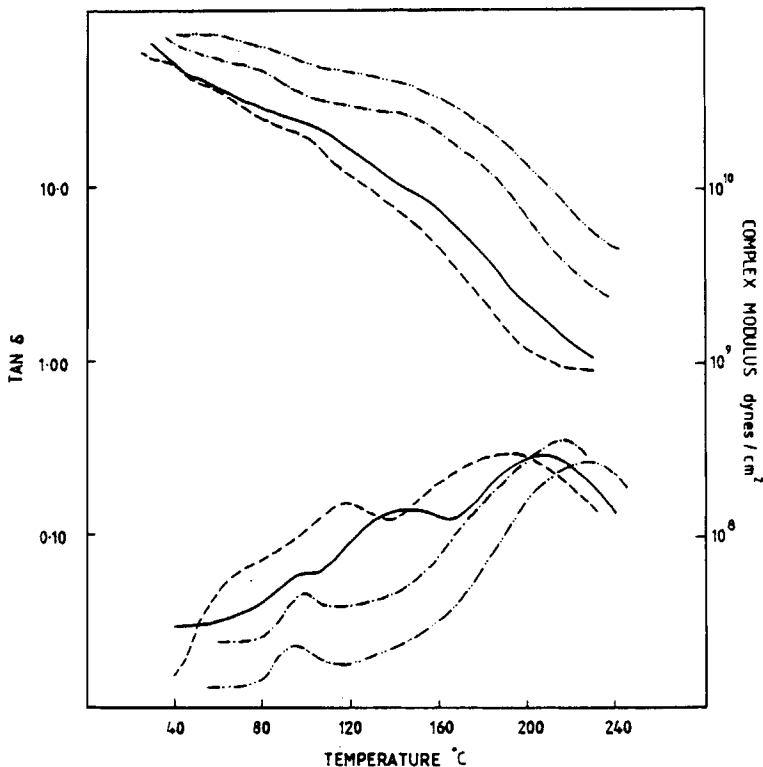


Fig. 11. Changes in dynamic mechanical properties with aging for Adhesive A. (---) Initial material; (-·-) 8 weeks; (—) 16 weeks; (- - -) 26 weeks. Upper set of curves, complex modulus; lower set of curves  $\tan \delta$ .

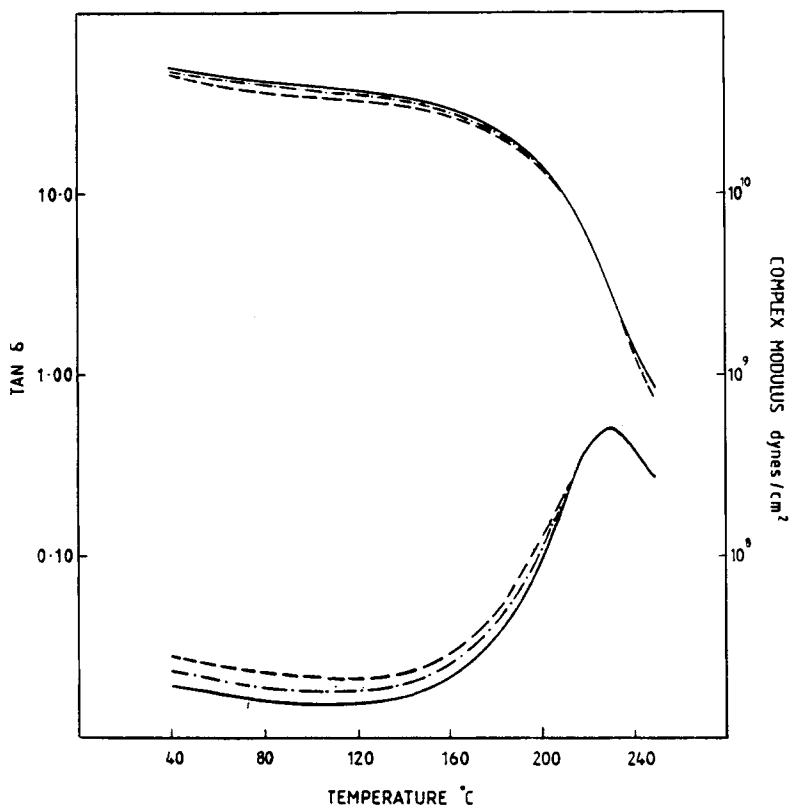


Fig. 12. Changes in dynamic mechanical properties with aging for Adhesive B. (—) Initial material; (---) 12 weeks; (-·-) 20 weeks. Upper set of curves, complex modulus; lower set of curves,  $\tan \delta$ .

and complex modulus curves. The maximum in the  $\tan \delta$  curve is reduced from about 225°C for the initial (unaged) material to about 185°C for adhesive aged for 26 weeks at room temperature. Similar substantial shifts to lower temperatures together with changes in the general shape are evident in the complex modulus curves. Clearly,  $T_g$  has been substantially reduced by the chemical changes occurring during aging.

The peak in the  $\tan \delta$  curve at 95°C is not associated with moisture loss since it is little altered by reheating. The origin of this, and of the other additional transitions discernible in the curves for aged samples, is the subject of further investigation.

In contrast, the dynamic mechanical properties of Adhesive B as elaborated by this technique are little altered by aging. The fact that this adhesive contains approximately 25% of a poly(ether sulphone) is a complication since the  $T_g$  of such materials is commonly about 225°C.<sup>10</sup> Apart from a suggestion of a shoulder on the  $\tan \delta$  curve at about 180°C, the samples are essentially unaltered by 20 weeks aging at room temperature.

Considering these results in relation to the high-temperature performance of these adhesives, and bearing in mind the additional curing effects referred to above, it is plain that, in the tensile shear testing at 177°C of the samples aged for shorter times, the adhesive was near its  $T_g$  but that in testing the samples

aged for longer times the adhesive was above its  $T_g$ . This accounts for the reduction in high-temperature performance before any changes in performance at lower temperatures was evident.

In regard to actual applications of these adhesives, both are qualified for use in structural aircraft applications for service to 200°C, even though the recommended cure temperature for each is around 177°C. It may be that, as a result of aerodynamic heating, further cure takes place *in situ*, leading to material of  $T_g$  higher than the original cure temperature. If aged adhesive is used, the margin of safety for high temperature use could be significantly narrowed especially if, for any reason, it is cured below 177°C.

Attempts have been made to relate directly a measure of some critical aspects of chemical composition of an adhesive (for example, intensity of the oxirane band near 910  $\text{cm}^{-1}$  in the infrared spectrum) to its performance (tensile-shear strength of lap joints for example).<sup>6,11</sup> Such attempts underestimate the chemical complexity of these systems and the diversity of possible reactions. However, in the case of adhesives containing the moisture-sensitive *N*-glycidyl aromatic amine moiety monitoring of the extent of hydrolysis by liquid chromatography is recommended.

### Durability of Bonded Joints

An indication of the effect of adhesive aging on joint durability was obtained by testing single overlap joints, at ambient temperature and 177°C, after they had been immersed in water at 40°C for 1000 h (Figs. 13 and 14).

For Adhesive A the water soak substantially modifies the tensile-shear strength of joints (Fig. 13). In the case of joints tested at 177°C, the magnitude of the effect is such as to obscure any additional susceptibility to the water environment which prior aging of the adhesive might induce. Clearly, the high temperature performance of joints made with this adhesive is quite intolerant of warm, moist

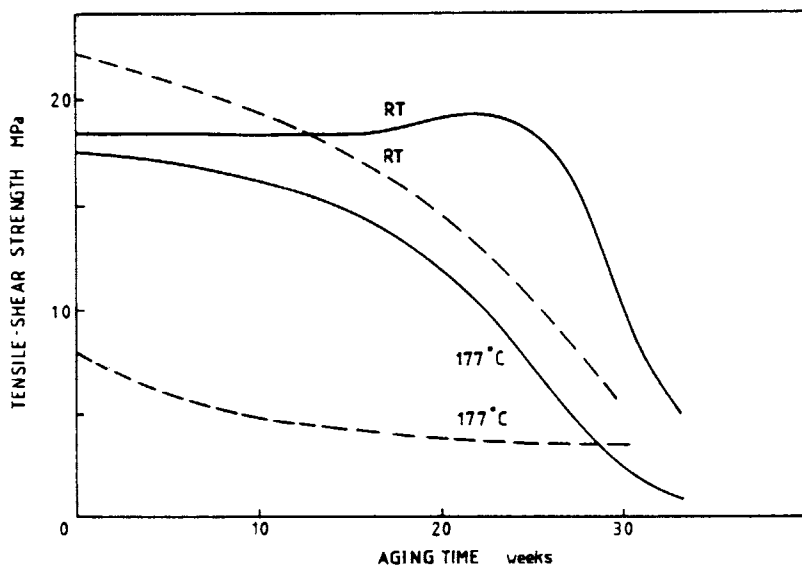


Fig. 13. Effect of water soak on tensile-shear strength of Adhesive A joints. (—) Aged material; (---) aged + water soak. Test temperature as indicated.

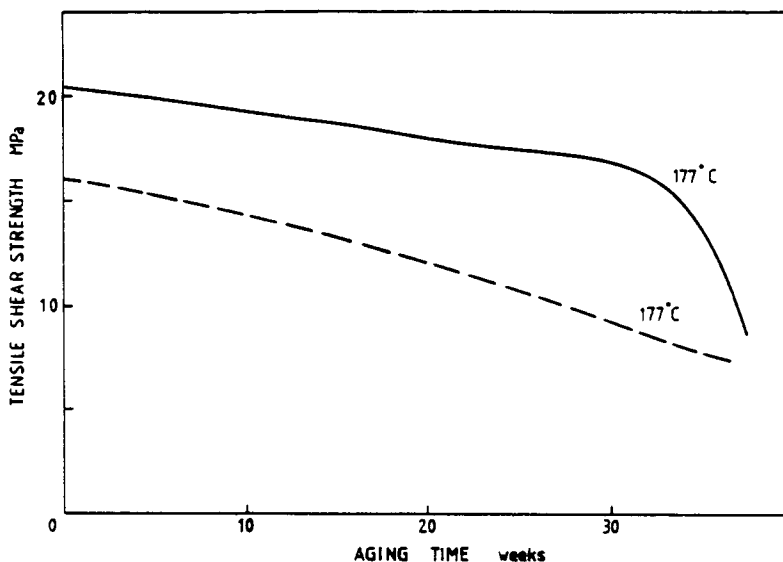


Fig. 14. Effect of water soak on intensity-shear strength of Adhesive B joints. (—) Aged material; (---) aged + water soak. Test temperature as indicated.

environments. In the case of joints tested at ambient temperature, the initial tensile-shear strength value is higher than that of their unsoaked counterparts. This is ascribable to a plasticizing effect of absorbed moisture. However, the overall trend is that joints made with aged adhesive are increasingly adversely affected by the water environment. Adhesive B is also affected in a similar way, but, to a somewhat lesser extent, in that the tensile-shear strength at 177°C is reduced by about a quarter, rather than about half (Fig. 14).

## CONCLUSIONS

The rate of change of various chemical and physical properties and of the mechanical performance of two epoxy-based adhesives during room temperature aging was found to be significantly different. Both systems contain the moisture sensitive compound triglycidyl(4-aminophenol). It is probable that material corresponding to this compound with all three epoxide groups hydrolyzed is eventually formed under the aging conditions. The greater rate of reduction of epoxide content and of solubility displayed by Adhesive A is consistent with the greater moisture sensitivity of the less pure grade of this epoxy compound.<sup>2</sup> Minor contributions to the overall greater stability of Adhesive B may arise from other differences in composition of the two adhesives.

The reduction in the mechanical performance of Al-Al joints made with aged adhesive, especially at high temperatures, is a consequence of the reduced epoxide content, resulting in a matrix of lower  $T_g$ . Joints made with both these adhesives were found to be quite intolerant of a warm, moist environment.

The advantages of using high purity resins as a means of maximizing shelf life are clearly demonstrated.

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