# Aging and Performance of Structural Film Adhesives. III. Effect of Humidity on a Modern Aerospace Adhesive*

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## Synopsis

The aging of an uncured, DGEBA-based commercial film adhesive exposed to high humidity at 40°C was monitored by high performance liquid chromatography (HPLC), thermal analysis, solubility, flow, and mechanical testing of joints. DGEBA and brominated DGEBA resins, and representative mixes of these were hydrolyzed in vitro. It is suggested that the major reaction at 40°C is polymerization, which is accelerated by moisture and leads to a crosslinked structure different to that resulting from normal cure. The poorer adhesive performance after aging is mainly the result of reduced resin flow during joint formation, although there is some contribution from the hydrolysis of epoxide groups which leads to lower crosslink density in the cured adhesive. The softening point of the uncured material and $T_g$ of the cured material are useful indicators of the quality of this adhesive which, compared to some earlier formulations, has improved resistance to these conditions.

## INTRODUCTION

In recent times the effect of moisture on uncured film adhesives and fiber-reinforced composite prepregs has received some attention. Concern has centered on the possibility of the changed processing behavior of these materials after exposure to high humidities causing such effects as higher levels of porosity and reduced performance of the cured material.[1-8]

It has been shown that the amount of moisture taken up by various adhesives differs greatly depending on the particular formulation.[3,4,6,7,9] Further, certain types of epoxy resin are inherently more susceptible than others to hydrolysis of the epoxide moiety.[10] Hydrolysis results in a reduction of the cross-link density, when the resin is subsequently cured, and thus a lower glass transition temperature $(T_g)$ of the cured material. Epoxy resins of reduced moisture susceptibility have been sought, and halogenated resins have been found to show promise.[11,12]

In the present work a newer, 120°C curing film adhesive, said by the manufacturer to have improved moisture resistance, has been characterized and examined during aging at 40°C and 96% relative humidity (RH). The changes in various chemical and physical properties occurring before cure, the progress of the cure reaction, and the adhesive properties of the cured

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material have been assessed and compared with those of material aged for the same time in dry conditions.

## EXPERIMENTAL

The adhesive used in this study was in the form of a supported film, weight 0.29 kg/m² (0.06 lb/ft²). It was stored before use at −18°C. One of the manufacturer's recommended cure cycles, 1.5 h at 113°C and 0.34 MPa, was used throughout.

The various epoxy resins employed in this work were Epikote 828, obtained from Shell Chemicals (Aust) Pty. Ltd., DER 511 and DER 542, provided by Dow Chemical (Aust) Ltd and Epotuff 37-200, obtained from A. C. Hatrick Chemicals Pty. Ltd.

Fresh adhesive (with backing paper on one side only) was aged in an oven at 40°C. Samples were placed on the shelves for "dry" conditions and in a desiccator containing a saturated sodium sulfate solution (to give approximately 96% RH) for "wet" conditions. Sampling was carried out at suitable intervals over 500 h.

In hydrolysis studies, resin (8 g) was heated under reflux in 100 mL water containing 0.1 mL 4 $M$ hydrochloric acid, and sampled at convenient intervals for subsequent HPLC analysis of the principal oligomer content.

For HPLC, a Spectra-Physics 8700 ternary solvent delivery system was used in the reverse-phase, linear gradient elution mode with combinations of tetrahydrofuran (THF), acetonitrile, and water as solvents and Zorbax columns—either ODS analytical or CN semipreparative. The ultraviolet (UV) detector was either an Altex model 153 or Waters model 481 set at various wavelengths.

For thermal analysis a Du Pont 1090 Thermal Analyzer was used with the 910 Differential Scanning Calorimeter (DSC) cell and a modified 941 Thermal Mechanical Analyzer (TMA). DSC curves were taken under nitrogen at heating rates of 5, 10, or 20°C/min. Low temperature curves were obtained by cooling the DSC cell, with liquid nitrogen in the stainless steel can, from above the glass transition temperature, and reheating at 10°C/min without moving the can. Isothermal curves were obtained by inserting the sample into the preheated cell. The samples (8–12 mg) were contained in crimped aluminium pans. TMA curves were obtained on single thicknesses of cured adhesive at 5°C/min. Initial heating to 150°C with the hemispherical (2.5 mm diameter) probe loaded with 10 g gave a penetration curve; expansion curves could be obtained by allowing the sample to cool at the natural rate—without disturbing the probe—and then reheating. Du Pont software was used in curve analysis.

Flow of the adhesive during cure was assessed by curing a 50 mm diameter disc of adhesive between release sheets in a heated platen press. The percent flow was calculated from the mass of material outside the original area.

Adhesive joints for T peel and tensile shear strength measurements were made with 0.5 and 1.6 mm type 2024 T3 Alclad aluminium sheet, respectively. Surface preparation in each case was a vapor degreasing with 1,1,1-trichloroethane followed by a chromic acid etch. No primer was used. Joints were made in a heated platen press. Joint geometry and test methods were in

accord with standard procedures.[13] The testing was accomplished with a model TT-C-L Instron tensile testing machine.

## RESULTS

### Characterization

The composition of the adhesive was found, by a combination of chromatographic and spectroscopic procedures, to be based on diglycidyl ether of bisphenol A (DGEBA) resins, as shown in Table I and Figure 1. It is of interest that the flexibilizer is poly(tetramethylene oxide) rather than the more commonly used carboxy-terminated butadiene acrylonitrile (CTBN) elastomers, and that both dicyandiamide (dicy) and the adduct of 2,4-toluene diisocyanate and dimethylamine (TDI/DMA) are present as the curing system. It is assumed that the toughening agent was pre-reacted with epoxide during formulation as we were unable to fractionate this component for more comprehensive analysis.

### Effects Prior to Cure

#### *Hydrolysis*

The possibility of hydrolysis of DGEBA epoxides in adhesive formulations under warm/wet conditions has been demonstrated previously.[14] The rate and extent of hydrolysis in the present material were examined by HPLC (Figs. 2–4) which shows that hydrolysis of DGEBA proceeds at 40°C in the "dry" state (utilizing the adhesives own water content) and considerably faster and to a greater extent at 96% RH.

The present adhesive contains a significant proportion of brominated DGEBA which is added to decrease the water uptake in cured epoxies.[11] It was therefore interesting to see whether the addition would improve the moisture resistance of the uncured formulation. The hydrolytic stability of the brominated and unbrominated DGEBA resins shown in Table II were assessed in weakly acidic boiling water. Figure 5 shows the relative rate of disappearance of the principal nonbrominated material (monomer, n = 0). Figure 6 shows the corresponding consumption of brominated DGEBA (the

TABLE I
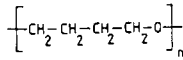Overall Composition of the Adhesive

Low MW DGEBA resin
High MW brominated DGEBA resin
Poly(tetramethylene oxide)
Dicyandiamide
Adduct of 2,4-toluene-diisocyanate
  and dimethylamine
Polyester support

Water
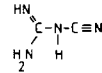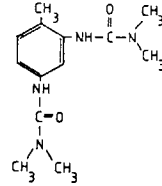Na, Cl, Si, S, Fe, Ti, I, K  } traces
Red dye
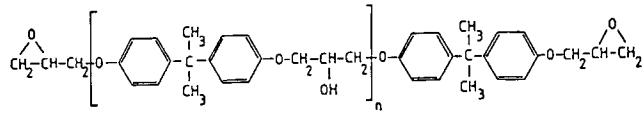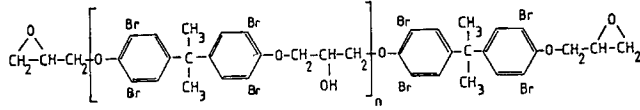
DGEBA

Brominated DGEBA

Poly (Tetramethylene oxide)

TDI/Dimethylamine Adduct

Dicyandiamide

Fig. 1.   Formulae of identified compounds.



433 hours wet

433 hours dry

control

DGEBA (Peak A)

DGEBA (Peak B)
Half hydrolysed

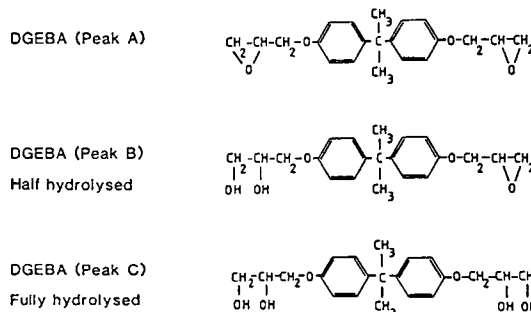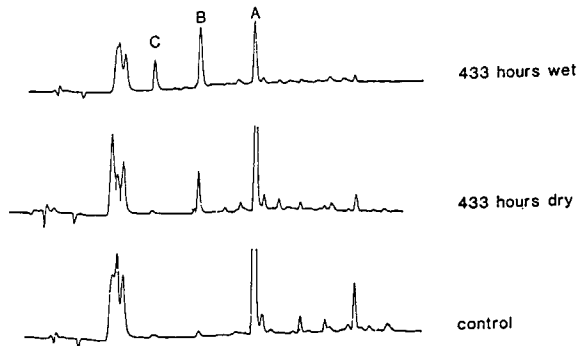DGEBA (Peak C)
Fully hydrolysed

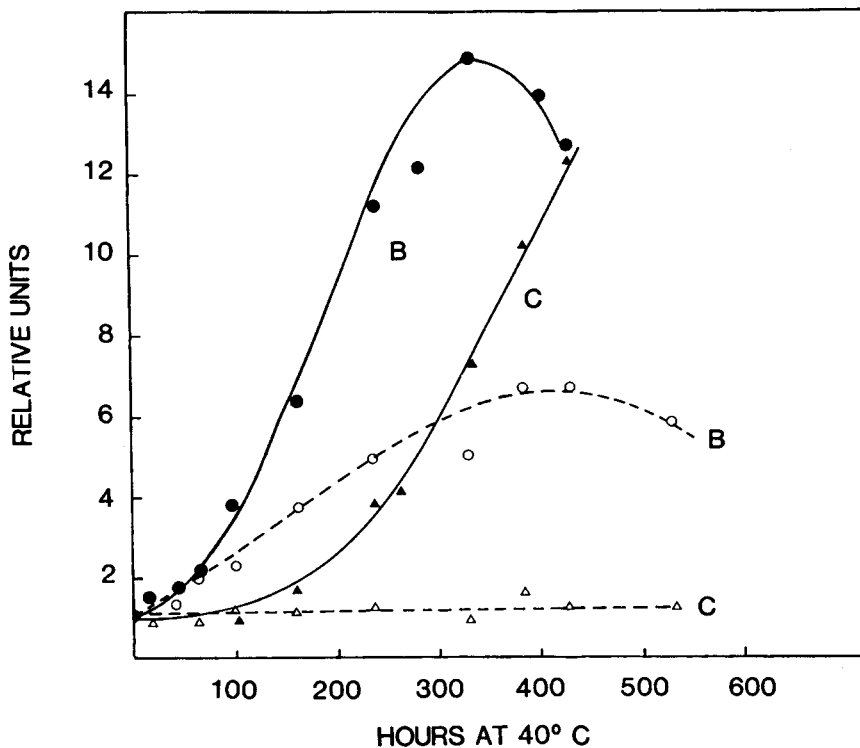Fig. 2.   HPLC/IR identification of hydrolysis products.

Fig. 3. The development of DGEBA hydrolysis products (B, C; Fig. 2) as a function of aging time. (▲ \ , ●) wet; (△, ○) dry.
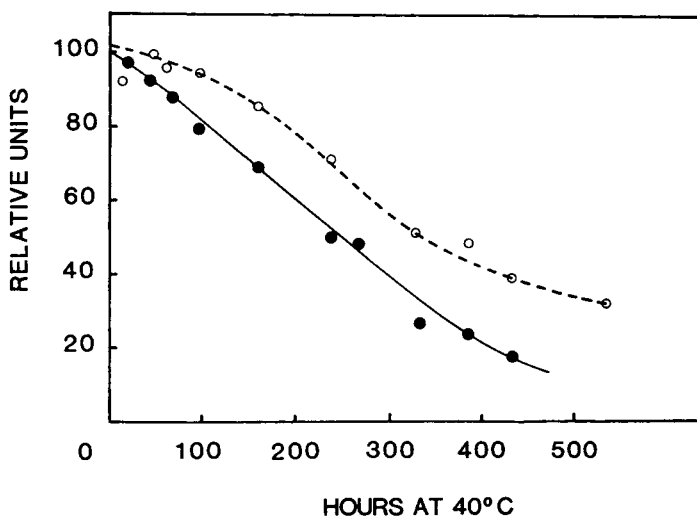


Fig. 4. The effect of aging on DGEBA (A; Fig. 2) content (●) wet; (○) dry.

TABLE II
DGEBA Resins for Comparative Hydrolytic Stability Studies

| Resin | Epoxy equivalent weight[a] (g/eq) | Bromine content[a] (wt %) | Manufacturer |
|---|---|---|---|
| Epikote 828 | 185–192 | — | Shell |
| DER 542 | 330–380 | 44–48 | Dow |
| DER 511 | 445–520 | 18–20 | Dow |
| Epotuff 37-200 | 245–265 | 24 | Reichhold |
| 828/542 | 250–290 | 23 | (50 : 50 mix by weight) |

[a] Data from manufacturers' brochures.

monomer, except for DER 511 in which the principal material is oligomeric, probably n = 2). Since DER 542 is fully brominated, it does not appear in Figure 5 and similarly Epikote 828, containing no bromine, does not appear in Figure 6. Clearly, tetrabromo-DGEBA is substantially more stable toward hydrolysis than its nonbrominated analogue.

The stability of mixed resins is of interest. It is seen (Fig. 5) that the hydrolytic stability of Epikote 828 is greatly increased by the presence of the DER 542, whereas the stability of DER 542 is substantially diminished by the presence of Epikote 828 (Fig. 6). The reason for this is uncertain, but presumably the concentration and reactivity of water in the 828/542 mix is intermediate between that in the individual components.
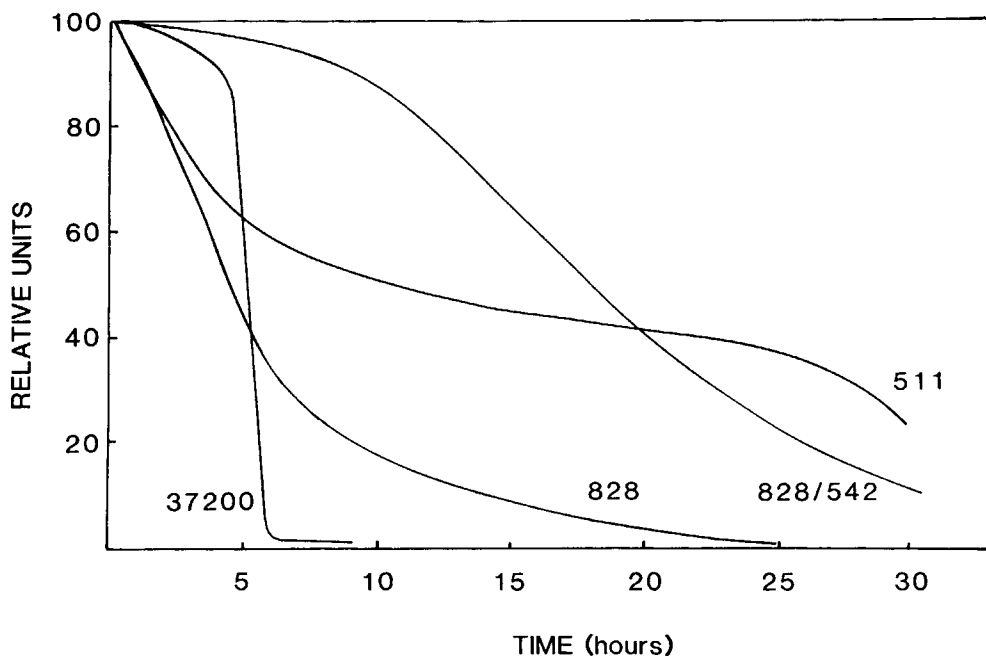


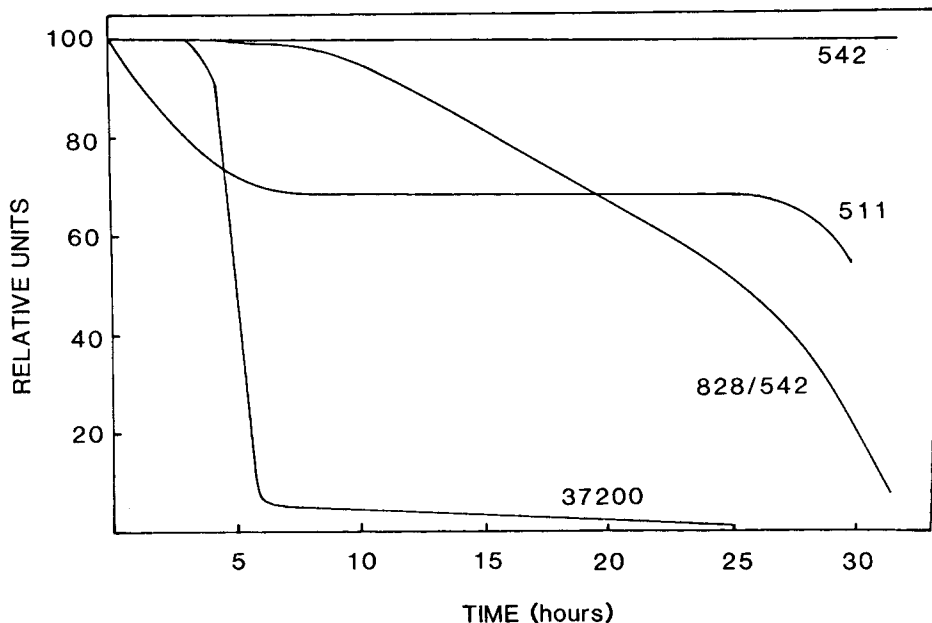Fig. 5. Hydrolysis of model systems: relative rate of disappearance of monomeric, nonbrominated epoxy resin.

Fig. 6.   Hydrolysis of model systems: relative rate of disappearance of monomeric, brominated epoxy or most abundant form, n = 2 (511).

In the case of Epotuff 37-200 (which has a very similar chromatogram to that of the 828/542 mix), the expected stability is seen for the first few hours, but then there is very rapid hydrolysis of all epoxides. In contrast, the DER 511 shows a pronounced stabilizing effect in the hydrolysis of both brominated and unbrominated components after significant initial reaction.

It has previously been remarked[2] that impurities in the resin can accelerate the hydrolysis, and the presence of brominated DGEBA has a significant effect on water levels in cured epoxies.[11] The basis of hydrolytic stability in formulated epoxy adhesives is clearly complex.

### Solubility

The adhesive will "advance" to some extent during 500 h at 40°C, and moist conditions might affect the rate of this polymerization. A small difference in the solubility of wet- and dry-aged adhesives seen after 200 h (Fig. 7) is indicative of such an effect.

Because the adhesive components, with the exception of the support, are virtually completely soluble in THF, a (undetermined) degree of advancement must take place before there is a significant insoluble fraction. The technique is thus unable to distinguish between batches in the early stages of aging.

### Softening Point

Advancement would also be expected to raise the softening point, although not significantly above the exposure temperature. The long exposure effectively anneals the samples, and to obtain comparable DSC curves the samples were heated through the transition (a distinct sharp endotherm after long
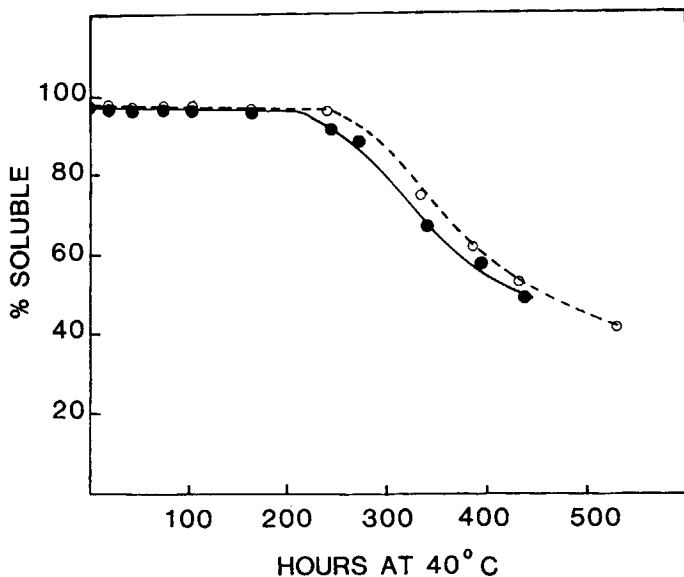
Fig. 7. The effect of aging on solubility in tetrahydrofuran. (●) wet; (○) dry.
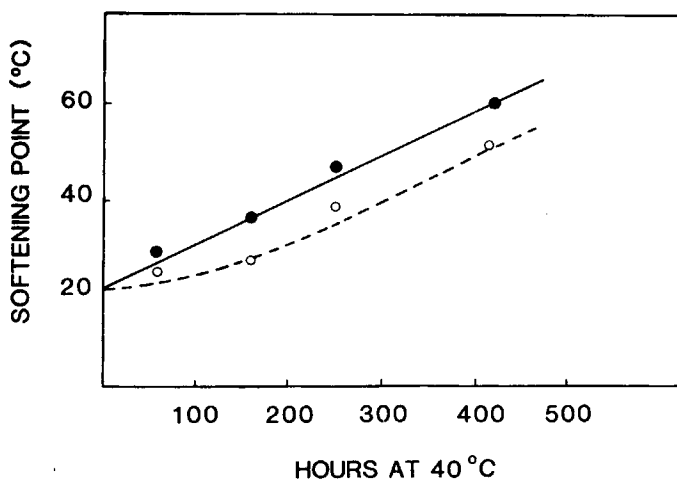


Fig. 8. The effect of aging on the softening point (end of DSC transition) of the uncured adhesive. (●) wet; (○) dry.

aging) and then cooled rapidly to $-40°C$ before reheating. Figure 8 shows the end of the glass transition, the most easily determined point on the DSC curve. There is slower change during the early stages under dry conditions.

## Effects During Cure

### Flow

The extent of adhesive flow accompanying cure decreased rapidly with aging time at 40°C (Fig. 9), but the difference between wet and dry aging conditions was relatively small.

Fig. 9.  The effect of aging on flow. (●) wet; (○) dry.

Conflicting results have been reported for the effect of moisture absorption on the extent of flow accompanying cure.[3,4,6] The effect appears t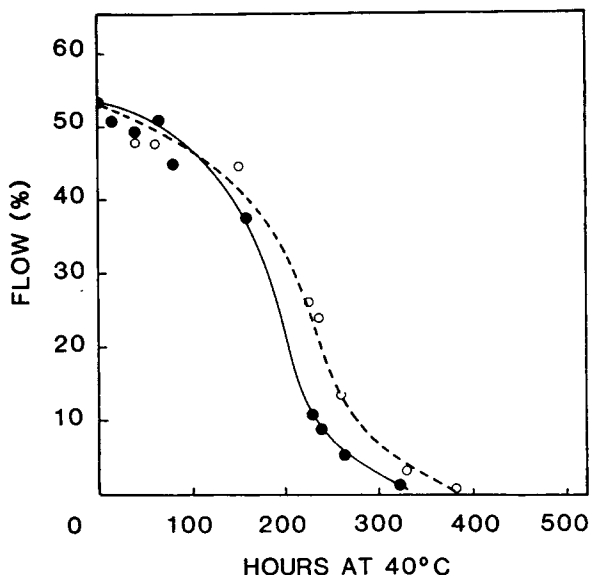o depend on the particular formulation; plasticization by absorbed water may facilitate flow; on the other hand, if the cure is accelerated by moisture then the time for flow during heat up may be severely curtailed.

Here the kinetics of cure appear insensitive to age or moisture (see below), and a relatively constant level of moisture present during cure should be established early in the aging. Therefore, the increasing advancement of the resin (leading to higher viscosity and softening point) will be the dominant factor in determining flow.

*Cure Kinetics*

Typical DSC curves for the cure (Fig. 10) show a single exotherm, and a subsequent endotherm which is attributed to the melting of residual dicy. Further exothermic activity above 220°C may be due, at least in part, to the decomposition of this unreacted dicy. The lack of resolution of cure and melt, which contributes to the difficulty in interpreting these dynamic DSC curves, is minimized by slow heating rates (5°C/min or less), but these give low signals which are inappropriate for extensively aged samples. The compromise rate of 10°C/min was chosen for comparisons. The results are given in Table III.

Isothermal DSC of the adhesive (control, 65 and 433 h wet aged) at 120°C showed reductions in the heat of cure comparable to those in dynamic DSC, but only slight changes in the time to maximum rate of reaction, and time to complete reaction. The major variation was in the $T_g$ of the cured resin, which is more appropriately measured on samples resulting from the flow measurements.
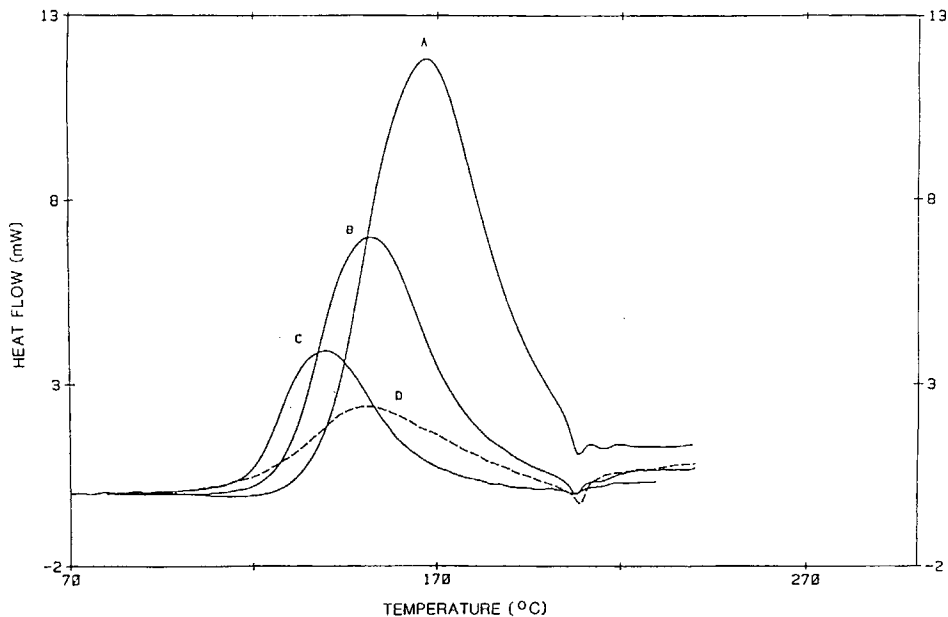
Fig. 10. DSC cure of adhesive (normalized to 10 mg samples): "as received" (A) 20°C/min; (B) 10°C/min; (C) 5°C/min; (D) after 433 h wet aging, 10°C/min.

TABLE III
Effect of Aging on DSC Cure

| | Heating rate (°C/min) | Aging time (h) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Wet | | | | | Dry | | | |
| | | 0 | 65 | 161 | 241 | 433 | 65 | 161 | 116.5 | 433 |
| $T_{onset}$ [a] | 5 | 119 | 118 | | 117 | 117 | | | 116.5 | 116 |
| $T_{max}$ [b] | | 140 | 140.5 | | 141.5 | 139.5 | | | 137.5 | 137 |
| $\Delta H_r$ [c] | | 164 | 164 | | 127 | 71 | | | 152 | |
| $\Delta H_f$ [d] | | 1.2 | 1.5 | | 1.6 | | | | 1.6 | |
| $T_{onset}$ | 10 | 128 | 126.5 | 127 | 126 | 120 | 125 | 127 | 125 | 124 |
| $T_{max}$ | | 151.5 | 153 | 153 | 152.5 | 150 | 149 | 151 | 149 | 149 |
| $\Delta H_r$ | | 167 | 165 | 144 | 119 | 74 | 167 | 168 | 141 | 107 |
| $\Delta H_f$ | | 1.1 | 1.2 | 1.2 | 1.4 | 1.9 | 1.2 | 2.0 | 2.0 | 2.2 |
| $T_{onset}$ | 20 | 139 | | | | 133 | | | | 134 |
| $T_{max}$ | | 166.5 | | | | 162 | | | | 162 |
| $\Delta H_r$ | | 145 | | | | 53 | | | | 98 |
| $\Delta H_f$ | | | | | | 1.9 | | | | |

[a] $T_{onset}$ = extrapolated onset of cure (°C).
[b] $T_{max}$ = temperature of maximum exotherm (°C).
[c] $\Delta H_r$ = heat of cure (J/g), to melting onset.
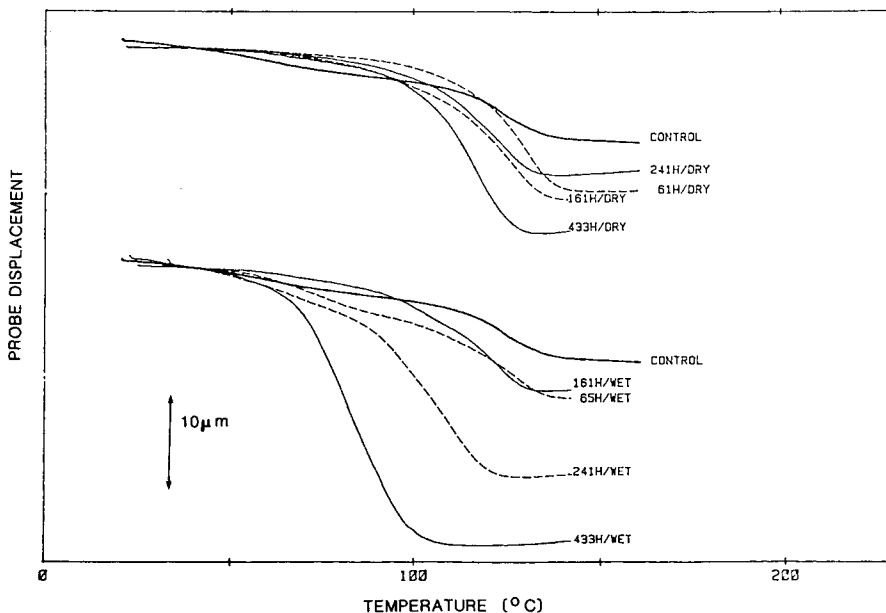[d] $\Delta H_f$ = heat of fusion of residual dicy (J/g).

Fig. 11.   Initial (penetration) TMA curves for aged adhesive; 5°C/min, hemispherical probe, 10 g load. The curves are displaced to coincide at 45°C.


## Effects After Cure

### Glass Transition Temperature

The glass transition of the cured adhesive, in respect to both thermal expansion and modulus (softening), was investigated by TMA on the cured "flow test" specimens. Curves are shown in Figure 11, and results are given in Table IV and Figure 12.

The additional penetration stage at a lower temperature (Table IV) was seen only in the control and first two wet-aged samples, but may be more evident under different TMA conditions. Dry-aged materials showed no indication of this effect.

Although many factors contribute to the variability of the initial TMA curves, the extrapolated end of the penetration can be determined more readily and consistently than the expansion $T_g$, which is generally 20°C lower.


TABLE IV
TMA of Aged Adhesive

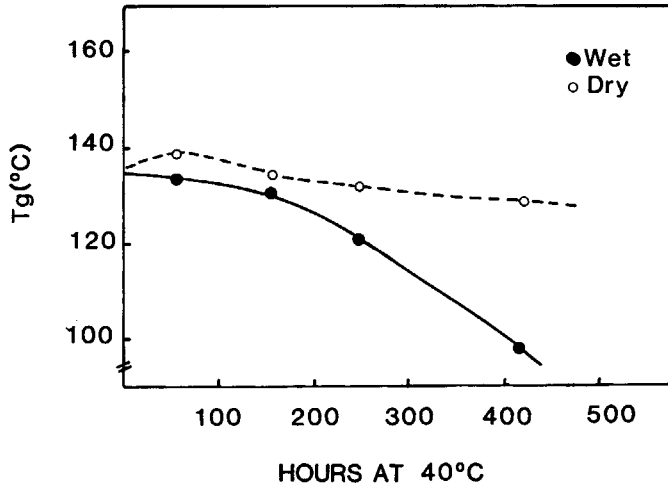| Sample age (h) | 0 | Wet | | | | Dry | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 65 | 161 | 241 | 433 | 65 | 161 | 241 | 433 |
| Temperature of max. penetration rate (°C) | 64 124 | 75 129 | 70 123 | 112 111 | 82 | 130 | 126 | 125 | 119 |
| End of penetration (°C) | 134 | 133 | 130 | 119 120 | 97 | 138 | 133 | 133 | 128 |
| $T_g$ (expansion) (°C) | 112.5 | | | 100 | | | 112 | 113 | 108 |

Fig. 12. Effect of aging on $T_g$ (end of penetration) of cured adhesive (flow test sample). (●) wet; (○) dry.

The end of transition determined in this way agrees well with that determined by reheating the samples cured during isothermal DSC.

### Peel Strength

The effect of using aged adhesive on the T peel strength of Al–Al joints is shown in Figure 13. Peel strength in film adhesives is often allied to the flow accompanying cure.[15] Here again peel strength and flow show similar behav-
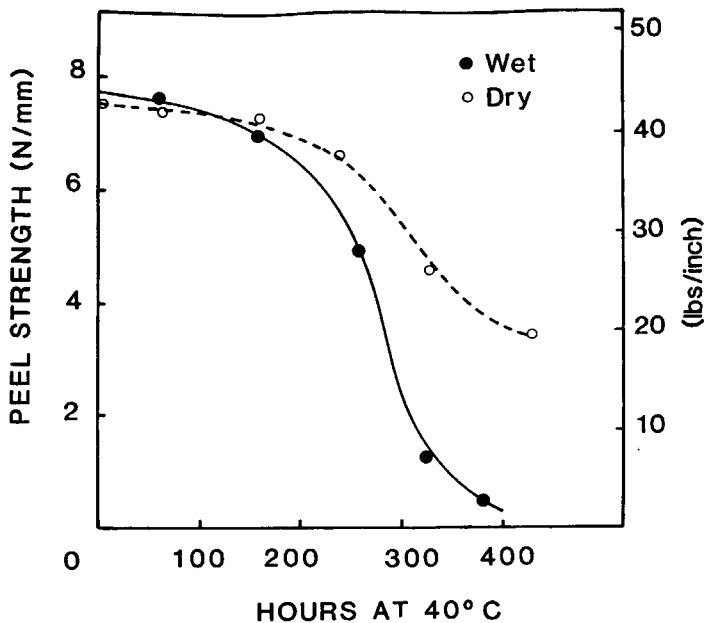


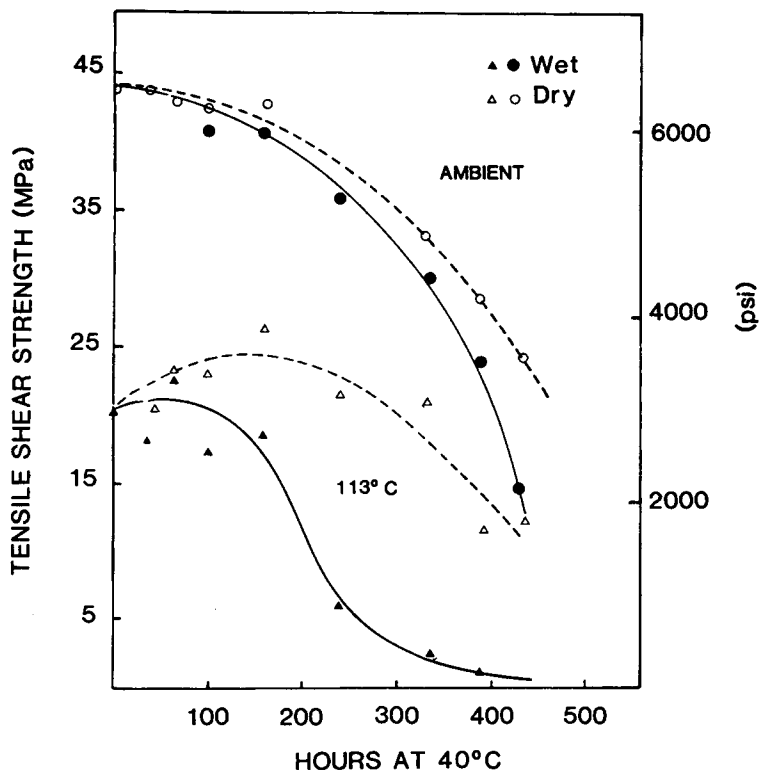Fig. 13. The effect of aging on peel strength. (●) wet; (○) dry.

Fig. 14. The effect of aging on lap shear strength tested at ambient and 113°C. (▲, ●) wet; (△, ○) dry.

ior, and in both, a gradual initial drop precedes a more significant reduction, with differences between wet and dry aging evident after about 150 h.

### Tensile Shear Strength

The tensile shear strength of Al–Al lap joints made with aged adhesive, measured at ambient temperature and at 113°C, are shown in Figure 14. Part of the drop in the values at ambient temperature may be due to the peel strength reduction at the longer aging times, since at tensile shear loads of above about 25 MPa the Al adherends distort, thereby introducing a significant peel component into the test. In contrast to the other results, the tensile shear strength of joints tested at 113°C shows qualitative differences between wet- and dry-aged materials. The major factor to be considered is the effect of aging on the $T_g$ (Fig. 12). Joints made with wet-aged adhesive perform badly because the test temperature is near the depressed $T_g$ of this material, but dry aging has little effect on the $T_g$. The increase in tensile shear strength suggests an increase in flexibility of the adhesive thereby better resisting the peel component in the test.

### DISCUSSION

The aging of the adhesive in wet and dry conditions has been followed by changes in various chemical and physical properties of the uncured and cured

adhesive. Generally, the changes are gradual at the outset and accelerate rapidly after about 200 h, and in most cases they are more pronounced in moist conditions. The question then arises as to whether moisture merely accelerates the changes, or whether additional mechanisms are involved, since the "as-received" material does contain some moisture, about 0.4%. From other work[9] it can be expected that under the two aging conditions the moisture content will rapidly increase to about 1.2% in the moist conditions, and decrease to 0.2–0.3% (depending on ambient RH and hence variable) in the "dry" conditions.

The role of moisture during aging should also be distinguished from the role of moisture during cure. Pike et al.[6] looked at the effect of moisture on the cure of a dicy/DGEBA adhesive and noted plasticization of the uncured material, modification of the curing agent, and a rapid (6 h) equilibration of water content. In their (170°C) system water was lost early during heat-up (ca. 100°C), and its presence was not thought to influence the actual cure. In the present case there is little difference between dry- and moist-aged material during the earliest aging when the major difference in water content is quickly established. It follows that moisture has relatively little effect during cure, that the changes occur to the uncured adhesive, and that advancement, hydrolysis, and possible modification of the curing system can be considered.

There can be no direct estimation of the hydrolysis during aging. The HPLC analysis (Fig. 2) indicates the levels of monomeric DGEBA (A), the partial hydrolysis product (B), and the fully hydrolyzed product (C) with respect to "as-received" concentrations. The relative levels under dry and moist conditions can be compared, but absolute values are not available; and would be of little value. The hydrolysis product B is a reacting intermediate removed by further hydrolysis to C, and by reacting with at least one of the following, DGEBA monomer and oligomers, brominated epoxies, and curing agent(s). In addition, these and "normal" advancement products can themselves be hydrolyzed. Although the concentrations of B and water are low it is still surprising that there is no increase in the amount of C in the "dry" conditions.

The commercial adhesive is too complex for detailed analysis of the hydrolysis, and while it would be preferable to use genuinely dry conditions for aging, the presence of hydrolysis products in the "as-received" commercial adhesive would negate much of the advantage of drying it.

The main compositional differences between the uncured adhesives aged in different conditions are established in the first 150–200 h. This is true for both monomer (DGEBA) and total epoxide (which is presumed to be proportional to the heat of reaction) (Fig. 4 and 15), where after this time the actual rate of consumption is similar in both wet and dry conditions. The change in softening point of the uncured material (Fig. 8) follows the same trend, and the flow behavior (Fig. 9) can be reconciled to the same pattern if it is assumed that the lower moisture level in the dry-aged material, compared to the "as-received" and wet-aged materials leads to decreased plasticization.

In contrast, the cured adhesive peel strength and tensile shear strength at room temperature are not sensitive to conditions until later in the aging, and the $T_g$ of the cured adhesive is particularly sensitive to the aging conditions (Fig. 12). The differences between the wet- and dry-aged materials when
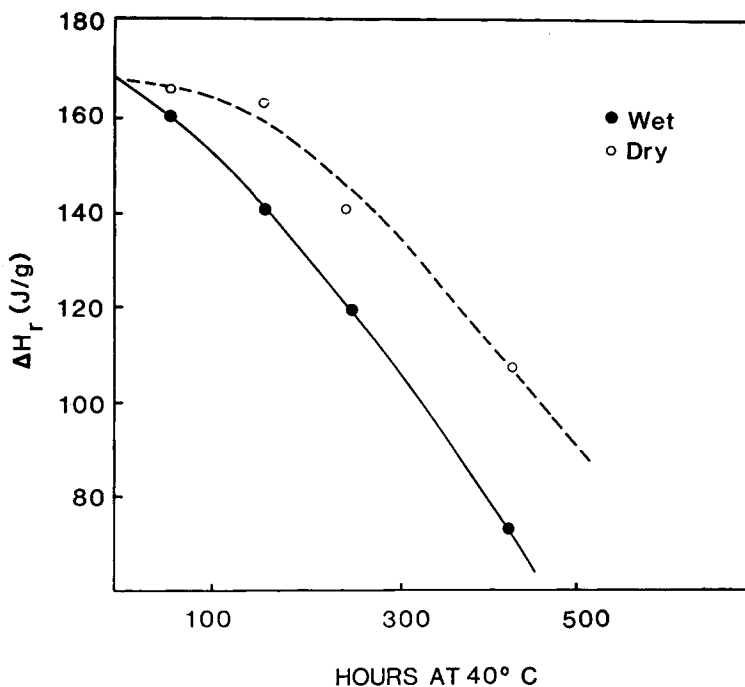
Fig. 15. The effect of aging on the heat of cure ($\Delta H_r$): (●) wet; (○) dry.

tested for tensile shear strength at 113°C can be largely explained by changes in $T_g$, the transition being broadened as well as lowered by aging.

A qualitative measure of the difference in cured wet- and dry-aged material is afforded by penetration TMA. The initial heating of a sample gives a TMA curve that will comprise expansion, penetration, stress relaxation, and sample accommodation of irregularities;[16] these complicate interpretation, particularly of expansion curves. Although penetration curves are quantitatively unreliable, the temperature indications are reasonably reproducible and adequate correlations are obtained between penetration TMA, DSC, and expansion TMA. In addition, the results (both TMA and DSC) of the adhesive cured in situ correlate well with the TMA (penetration) results on the "flow test" samples.

This leads to some confidence in the penetration results shown in Figure 11. The TMA curves are superposed at 45°C; penetration predominates and the curves should be more or less independent of the variable sample thickness (over the range 40–140°C expansion on reheat is no more than 6 $\mu$m, much less below $T_g$, compared to penetrations of 15–40 $\mu$m).

The modulus change over the glass transition is much greater in the aged samples, particularly in those aged in the wet; and there appears to be earlier penetration of the wet-aged material compared to the control and the dry-aged materials.

It could be argued that some of these differences are due to water absorbed in the samples; however this seems unlikely, as water would be expected to be desorbed during curing, particularly in the small samples used in thermal analysis. There is thus no ambiguity in the main measurement of end of
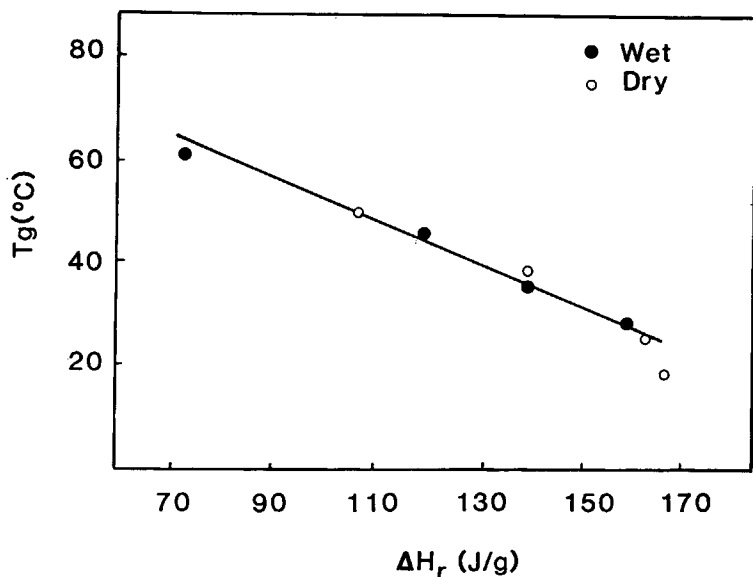
Fig. 16.   Correlation between softening point of uncured adhesive and heat of reaction on cure. (●) wet; (○) dry.

transition; it is genuinely lower and not by plasticization. The differences below $T_g$ are less certain, but all these "flow test" samples have had adequate time to equilibrate with normal humidity, and the curves should be comparable.

The balance of evidence favors a different structure for wet- as opposed to dry-aged adhesive, namely, the more rapid $T_g$ change, the greater loss of rubbery modulus and different penetration pattern below $T_g$, and the tensile shear results, in particular the initial increase in the high temperature values.

We suggest that hydrolysis of the epoxide group is not a major factor during aging in moist conditions because, unexpectedly, the plot of $T_g$ of the uncured adhesive against heat of reaction (Fig. 16) does not distinguish between wet and dry conditions. The increase in $T_g$ results from polymerization (by whatever mechanism) of the epoxide, hydrolysis would not be expected to contribute to increased $T_g$. The total consumption of the epoxide group is measured by reduction of the heat of reaction. Figure 16 shows that similar increases in $T_g$ accompany like decreases in epoxide content whether in wet or dry conditions, and therefore most of the epoxide must have polymerized, not hydrolyzed. Also, because both $T_g$ and heat of reaction change faster in wet conditions (Figs. 8 and 15), it follows that advancement is facilitated by moisture.

On the other hand, relatively little hydrolysis could significantly lower the cross-link density of the cured material and plots of peel strength and shear strength against either $T_g$ or heat of reaction of the uncured material do show a moisture effect. These latter properties of the adhesive are not sufficient to describe changes in the cured material.

The adhesive, which contains two epoxy resins and mixed curing agents, is designed for cure at 113 or 120°C. The range of reactions leading to polymer-

ization of the resin which can be postulated is therefore considerable. These will have differing energies of activation (and sensitivity to catalysis) so that the balance of reactions will depend on the temperature, and structures formed at lower temperatures may not be the same as those at the recommended temperature. We have found that the TDI adduct, used in conjunction with dicy in this adhesive, when used as the sole curing agent in another DGEBA-based adhesive, is capable of practical cures at 80°C.[17] Appreciable reaction of the DGEBA resin and this curing agent at 40°C would therefore be expected to be the most probable mode of polymerization.

A further consideration is raised by Pike's suggestion that a dicy (plus aromatic amine) hardener can react with moisture at low temperature to alter the course of subsequent high temperature cure.[6, 18]

Finally, the adhesive under study is complex, containing two curing agents, two epoxies, and a rubber adduct. At the later stages of aging there is little or no flow (Fig. 9), which suggests very substantial chain extension, if not gelation, while at the same time there is evidence of limiting insolubilization (Fig. 7). It is possible that either one or both of the brominated epoxy and the rubber are not participating in the advancement.

## CONCLUSIONS

The adhesive has been aged under moist (96% RH) and "dry" conditions. It is suggested that the major reaction is advancement by the DGEBA resin and the TDI adduct, and that this reaction is facilitated by moisture. On curing the aged material, the balance of reactions is different because of pre-reaction and consumption of some components, and because of different temperature dependencies of competing reactions. In addition, relatively small amounts of hydrolysis can lead to effective reduction in cross-link density. The relative contributions of these possibilities to the overall degradation of network structure and adhesive performance cannot be assessed in a complex mixture.

It is believed that after substantial aging the immediate causes for poor adhesive performance are: (a) a reduced flow because of higher softening point of the uncured material; and (b) a modified network structure and reduced cross-link density giving cured material of an inherently lower strength, and lower $T_g$. The measurement of flow or softening point of the uncured adhesive, and the $T_g$ of the cured adhesive would appear to offer the best assessment of the quality of this particular material, when the more demanding formation and testing of joints is not required.

Although this improved adhesive is affected by high humidity at 40°C, it performs better after wet aging than materials we have previously studied. The uncured adhesive can be exposed for some 200 h (8 days) with little effect on the mechanical properties of subsequent joints, although after longer times there is significant degradation of performance. Longer "out" times can be expected under less aggressive conditions.

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