

Aging and Performance of Structural Film Adhesives. IV. A Modified Epoxy with Improved Ambient Temperature Shelf Life

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SYNOPSIS

It appears that improved latency in nitrile epoxy adhesives can be achieved by replacing the commonly used urea accelerator with one of much reduced solubility but similar chemical activity. A new, commercially available film adhesive claimed to possess a shelf life of 1 year at 22°C, excellent resistance to humidity prior to cure, and a service temperature range of -55 to 120°C has been examined. Areas studied included characterization, cure kinetics, adhesive performance, and shelf life. Its composition was found to be a variant of the 120°C curing nitrile-epoxy systems using a urea-accelerated dicyandiamide cure. Two novel features were noted: the presence of bisphenol S and the urea 1,1'-*p*-phenylene-bis(3,3-dimethyl)urea. The relatively high shear strength found at elevated temperatures could be related to the adhesive's high T_g of 155°C resulting from the addition of bisphenol S and the improved room-temperature latency was due to the ultralow solubility of the urea accelerator. Good durability was obtained from aluminum joints prepared using a simple silane pretreatment. Aging experiments indicated a shelf life of at least 3 months at 23°C under both dry and wet conditions, and it is predicted that adhesives of this type of composition would be stable for at least 1 year at normal domestic refrigeration temperatures of 5–10°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Structural adhesive bonding is now extensively used in the manufacture and repair of both civil and military aircraft. Most adhesives for these applications are in the form of one-part, epoxy-based films with typical recommended maximum storage lives of only 6 months at -20°C or a few days at room temperature. Although the one-part form, which requires only the applications of heat and pressure to effect its cure, has significant advantages in terms of ease of application, its relative instability is of particular concern in Australia since all adhesives of this type are imported and must be transported over long distances and stored at subambient temperatures before use. A structural film adhesive with greatly enhanced ambient shelf life could be transported without re-

frigeration and used in locations without suitable cold-storage equipment.

In previous work¹⁻⁵ it has been shown that film adhesive formulations rely on latent catalyst/curing agents such as dicyandiamide and substituted ureas, for example, 4-chlorophenyldimethyl urea (Monuron), to limit advancement at low temperatures. However, aging experiments have confirmed their limited shelf life by showing that the cure reactions proceed slowly at ambient temperatures and are often accelerated by high humidity.

This paper examines a new, commercially available film adhesive claimed to possess a shelf life of 6 months at 32°C or 12 months at 22°C, excellent resistance to humidity prior to cure, and a serviceable temperature range of -55 to 120°C. The nature of the compositional changes from earlier adhesives, and their effect, has been determined together with cure kinetics, adhesive performance, and an assessment of shelf life covering both dry and wet conditions.

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EXPERIMENTAL

The adhesive used in this study was in the form of a supported film, weight 0.29 kg/m^2 (0.06 lb/ft^2). It was stored before use at -18°C .

For high-performance liquid chromatography (HPLC), a Spectra-Physics 8700 ternary solvent system was used in the reverse-phase, linear gradient mode with combinations of tetrahydrofuran (THF), acetonitrile, and water as solvents; a Zorbax ODS analytical column, and a Waters Model 481 UV detector set at various wavelengths.

Separations using gel permeation chromatography (GPC) were effected using an Altex 110A pump with a Waters R401 RI detector in series with an Altex 153 UV detector at 280 nm. Five Waters ultrastyrigel columns (1×10^4 , 1×500 , $3 \times 100 \text{ \AA}$) were used with THF as solvent.

Thermal analysis was performed with a DuPont Thermal Analyst 2000 fitted with a 910 differential scanning calorimetry (DSC) cell. Samples were placed in crimped aluminum pans and heated either isothermally or at $5^\circ\text{C}/\text{min}$ in static air, unless otherwise indicated.

In the shelf-life study, small squares of fresh adhesive (with backing paper on one side only) were aged in laboratory ovens at 23, 40, and 60°C . Samples were placed on the shelves for "dry" conditions and in a desiccator containing a saturated solution of sodium sulfate (to give about 96% RH) for "wet" conditions. Sampling was carried out at suitable time intervals. Epoxide content was monitored using HPLC and DSC to follow the disappearance of the monomeric diglycidyl ether of bisphenol A (DGEBA) and total epoxide, respectively.

Adhesive joints were made with 1.6 and 3.2 mm 2024-T3 Alclad aluminum sheets for single overlap shear and wedge test specimens, respectively. Cure was effected using a heated platen press. For lap shear strength, joint geometry and test methods were conducted in accordance with ASTM D1002-72. Wedge tests were performed according to ASTM D3762-79. Specimens were exposed to a controlled atmosphere of 96% RH at 50°C and crack growth was monitored at suitable intervals using a stereomicroscope.

For the acid-etching procedure, the aluminum was wiped with clean methyl ethyl ketone (MEK), vapor-degreased with 1,1,1-trichloroethane, immersed in a stirred chromic acid bath for 10 min at 65°C , washed with cold running tap water for 10 min, and, finally, dried at 65°C for 1 h. The etch composition was 3750 g water, 680 mL concentrated sulfuric acid, and 500 g potassium dichromate dihydrate. The

"seeded" etchant contained, in addition, 5 g per liter of copper sulfate pentahydrate.

In the silane treatment, the metal was wiped with MEK, vapor-degreased as above, grit-blasted with $< 230 \mu$ zircon sand, immersed for 20 min in 1% w/v epoxy silane solution, drained, and dried for 1 h at 110°C . The silane used was gamma-glycidoxypropyltrimethoxysilane supplied as Dow type Z6040. Solutions were prepared by adding 30 mL silane slowly with stirring to 150 mL 0.1% aqueous acetic acid and diluting the mixture to 3000 mL with clean methanol. The grit-blast-only treatment comprised the MEK wipe, vapor degrease, and zircon sand as described previously.

RESULTS AND DISCUSSION

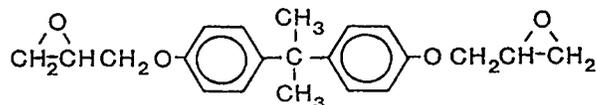
Chemical Characterization

Using a combination of HPLC and GPC (analytical and preparative), infrared analysis (IR), and mass spectrometry (MS), the adhesive was found to be based on a DGEBA resin as shown in Table I and Figure 1. The identity of the urea accelerator was confirmed by laboratory synthesis. Thus, the slow addition of excess dimethylamine (DMA) to a stirred solution of *p*-phenylene diisocyanate (PDI) in dry toluene produced an insoluble white precipitate with similar infrared and mass spectra and melting characteristics to the material isolated from the adhesive. The formulation is typical of the nitrile-epoxy, 120°C curing systems in being toughened with carboxyl-terminated butadiene-acrylonitrile rubber (CTBN) and cured with dicyandiamide (dicy) accelerated by a urea. However, 1,1'-*p*-phenylene-bis(3,3-dimethyl)urea—the adduct of *p*-phenylene diisocyanate and dimethylamine (PDI/DMA)—is novel and the presence of 2,2-bis(4-hydroxyphenyl)sulfone (bisphenol S) is of particular interest.

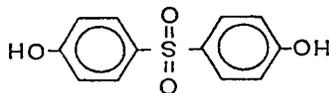
The bisphenol S was found in adducted form together with DGEBA and CTBN, and it is claimed by Klapprott et al.⁶ that this combination can be

Table I Adhesive Composition

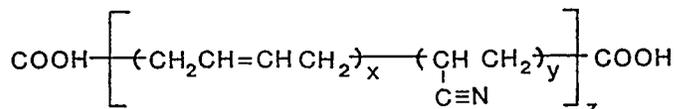
Low molecular weight DGEBA	Epoxy resin
Adduct of DGEBA, Bisphenol S, and CTBN rubber	Toughener
Dicyandiamide	Latent curing agent
1,1'- <i>p</i> -phenylene-bis(3,3- dimethyl)urea	Accelerator
Polyester mat	Support



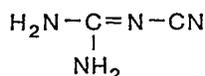
Diglycidyl ether of bisphenol A (DGEBA)



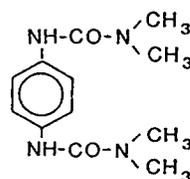
Bis (4-hydroxyphenyl)sulphone (Bisphenol S)



Carboxyl terminated butadiene acrylonitrile rubber (CTBN)



Dicyandiamide



1,1'-p-phenylene-bis(3,3-dimethyl)urea

Figure 1 Formulae of identified compounds.

used in adhesive compositions to produce improved toughness and high-temperature shear strength. In a study by Van Hoorn,⁷ it was shown that the polyhydroxyether produced from bisphenol S and its diglycidyl ether had a glass transition temperature (T_g) of 170°C, whereas its bisphenol A equivalent had a T_g of only 100°C. This significant increase was attributed to interaction by hydrogen bonding between hydroxyl and sulfonyl groups leading to greater chain stiffness. Thus, the presence of bisphenol S in the current system may well contribute to an improved high-temperature performance by raising its T_g .

Dimethyl-substituted urea accelerators are frequently added to DGEBA/dicy formulations in order to reduce the cure temperature from around 175 to 120°C. The cure mechanism of these systems is yet to be fully resolved, but there is general agreement that the urea provides a latent source of DMA that subsequently catalyses the dicy/epoxy reactions.⁸⁻¹³ Typical examples include 3-(4-chlorophenyl)-1,1-dimethylurea (Monuron), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron), and the adduct of toluene diisocyanate and dimethylamine (TDI/DMA). The urea found in the present ad-

hesive, PDI/DMA, is novel in that it has a much higher melting point ($\sim 300^\circ\text{C}$) and it is very insoluble, even in DGEBA resin. In contrast, those ureas named previously have melting points in the 150–200°C range, can be recrystallized from ethanol, and are readily soluble in DGEBA. It is therefore proposed that any gains in ambient shelf life have been achieved by using a urea accelerator that is significantly less soluble at lower temperatures than were the examples used previously.

Thermal Characterization

DSC curves of the adhesive obtained at 5°C/min were characterized by a single, sharp, apparently simple reaction exotherm beginning from about 110°C and completed by 200°C. Reheating the sample at 10°C/min showed that the T_g was 116–140°C (extrapolated onset to end). Under isothermal conditions, when the sample was added to the preheated cell, the autocatalytic reaction was sluggish at 100°C, taking 2 h to reach maximum rate, and was incomplete after 4 h. At 120°C, the maximum rate of cure was attained in 11 min and the vitrification limited reaction was complete within 1 h. The residual heat

of reaction of this sample was about 10% of the total heat of reaction. At 135°C, the reaction was complete in 40 min, there was no residual heat of reaction, and the T_g was 122–155°C.

The DSC results offer no explanation for the improved room-temperature latency of this adhesive. The extent of reaction at the peak maximum was dependent on the heating rate, and the plots of \log (heating rate) vs. inverse absolute temperature at various iso-conversion extents were neither linear nor parallel. Thus, the reaction kinetics are complex and provide an explanation for the difference already noted between the T_g of samples fully cured under dynamic and isothermal conditions. The apparent activation energy roughly calculated from these plots (5–20°C/min, 2.5–20% conversion) was in the range 70–100 kJ/mol and thus typical of the value expected for “normal” epoxy cure, which suggests that the latency does not lie in the bulk reaction.

To investigate further the function of the novel urea found in the present adhesive, thermal studies were conducted on mixtures of this accelerator and DGEBA, with and without dicy. Comparisons were made with similar mixtures based on typical urea accelerators found in “older” systems.

DSC curves were obtained for mixtures of DGEBA monomer (Shell X22) and Monuron (5 phr), TDI/DMA, or PDI/DMA (of the same DMA equivalence) in open pans, a condition not conducive to optimum reaction since it has been previously observed that the reaction of epoxides with dicy and/or urea accelerators is influenced by choice of open or hermetic pans.¹⁴ Clearly, in comparison to the

more commonly used ureas, although the reaction of PDI/DMA with epoxide required a higher temperature, it was not qualitatively different (Fig. 2). When crushed dicy (ca. 8 phr) was sprinkled on top of each mix, the observed synergistic effect (measured by the lowering of onset or peak maximum temperature) was greatest with the new accelerator (Fig. 3) and then only slight differences in reaction temperatures were seen.

Use of a hot-stage microscope showed that, whereas the “older” ureas were largely dissolved in X22 by 100°C, PDI/DMA was apparently not soluble. Hagnauer and Dunn¹⁵ measured the solubility of Monuron in Epon 828 as greater than 10% at 100°C, whereas in this work, PDI/DMA was isolated from the film adhesive by virtue of its extreme insolubility in THF. However, despite this insolubility, X22 slowly reacted at 120°C in the presence of PDI/DMA (which was not completely dissolved, and in less than stoichiometric proportions), so that after 1.5 h, the T_g had increased to nearly 90°C. It therefore seems probable that the latency of this adhesive does, indeed, lie mainly in the insolubility of the accelerator used—a physical rather than a chemical consideration.

The chemistry of these ternary systems is complex^{8–13} and a more subtle influence of the accelerator on the course of the reaction and structure of the product cannot be excluded. The general assumption is that DMA is produced either by reaction or, together with isocyanate, by decomposition of the urea and that it is the effective catalyst for both homopolymerization of the epoxide and its reaction

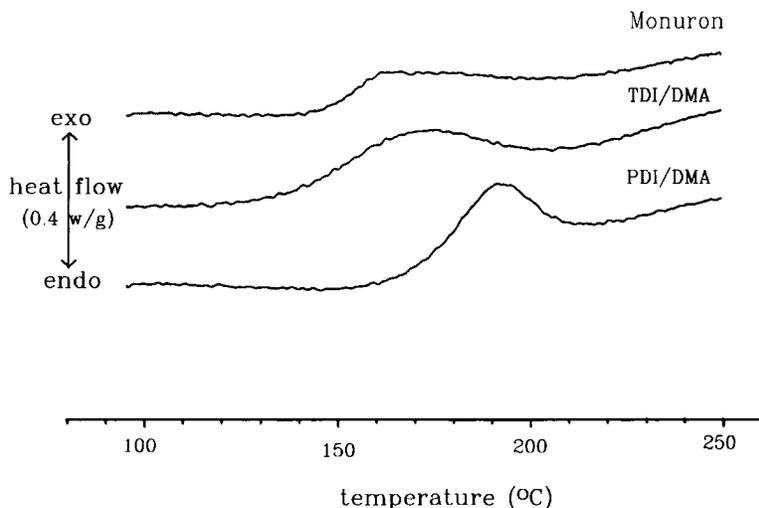


Figure 2 DSC curves of mixtures of pure DGEBA and (1) PDI/DMA (3.15 phr), (2) TDI/DMA (3.32 phr), and (3) Monuron (5.0 phr). Open pans, 5°C/min. Curves are displaced vertically.

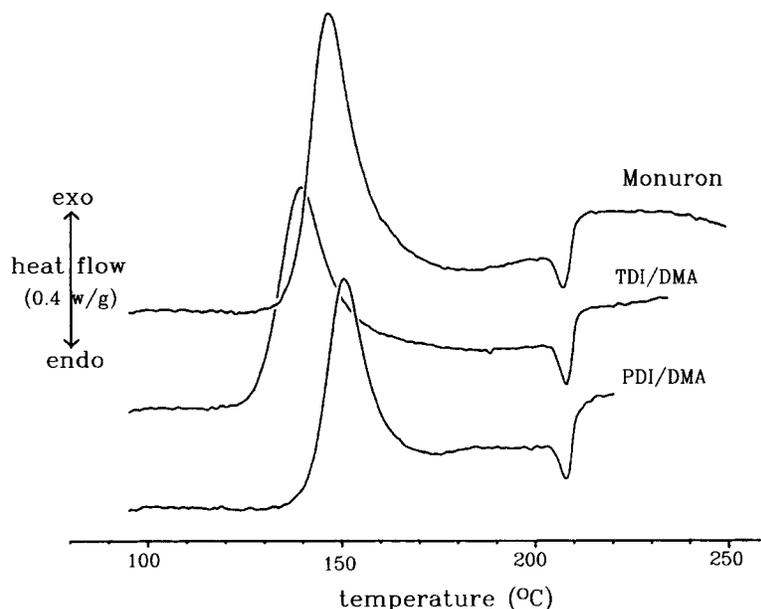


Figure 3 DSC curves of mixtures as shown in Figure 2 with dicy (~ 8 phr) sprinkled over sample. Conditions as per Figure 2.

with dicy. In experiments with model compounds, the formation of various intermediate structures has been reported; it is expected that the course of these reactions will be determined by the particular experimental conditions and reactant ratios. PDI/DMA has a high melting point (approximately 300°C) in a hermetic pan, although it decomposes before this in an open pan, possibly as a result of dissociation to biuret and/or isocyanurate, and is relatively insoluble compared to the more common urea accelerators that melt, decompose, and dissolve much more readily. However, the relative stability of these accelerators is not indicative of their chemical reactivity. Brockmann and Barwich¹¹ noted that TDI/DMA was a particularly effective accelerator because the incorporation of the diisocyanate moiety resulted in chain extension rather than termination and was therefore beneficial to the T_g of the product. The effect is probably small, but will also apply to the present urea that is derived from *p*-phenylene diisocyanate.

Adhesive Performance

The tensile shear strength of single aluminum lap joints prepared using three different surface preparation methods and tested at a range of temperatures after 1 h cure at 135°C is shown in Figure 4.

The chromic acid etch and epoxy silane treatments resulted in reasonably high ambient shear

strengths of 31.4 and 29.1 MPa, respectively, but as would be expected from a nonchemically prepared surface, the sandblast-only joints gave a significantly lower value of 23.7 MPa. At higher test temperatures, there was a gradual reduction in strength that could be related to the adhesive's fairly high ultimate T_g of about 155°C . Thus, at a test temperature of 140°C , both chemical treatments gave joint strengths exceeding 14 MPa. The ambient shear strengths of around 30 MPa are a little lower than those obtained from similar systems examined previously,^{4,5} and this observed drop could possibly be related to differences in peel strength, since at tensile shear loads exceeding about 25 MPa, the aluminum adherends distort and introduce a significant peel load into the test. The presence of bisphenol S in the present adhesive may confer increased chain stiffness after cure, which, in turn, leads to a higher T_g and improved high-temperature strength, but peel strength may be reduced to some extent.

The effect of cure temperature on chromic acid-etched lap joints tested at ambient is illustrated in Figure 5. Shear strength increases slightly as the cure temperature is increased from 120°C through 135°C to 149°C , the difference between extremes being about 15%.

Shelf-Life Study

Aging experiments on uncured adhesive conducted under both dry and wet (96% RH) conditions were

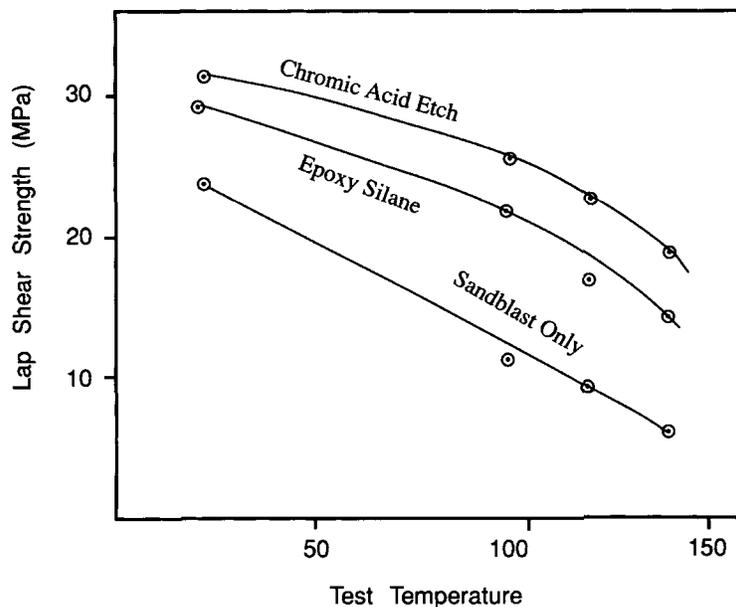


Figure 4 Lap shear strength as a function of test temperature after various surface pretreatments. Cure: 1 h at 135°C.

carried out isothermally at 23, 40, and 60°C. Figure 6 shows the relative depletion of monomeric DGEBA epoxide as a function of exposure time. Results indicate that at 23°C the adhesive is stable for almost 100 days in both conditions, after which consumption of monomeric DGEBA is more rapid in the humid atmosphere. At higher temperatures, the adhesive is less stable, especially when exposed to moisture: Thus, at 40°C, 15% of its epoxide content is lost after about 50 and 20 days under dry and wet storage, respectively, and at 60°C, under similar

conditions, this loss occurs after just 6 and 2 days. As has been shown previously,⁵ the increased rate of epoxide loss in the humid atmosphere can be attributed to the combination of epoxide hydrolysis and advancement.

Thermal analysis confirms these results: DSC curves showed that at 40°C the change in heat of cure was slow and, after 30 days, had been reduced by 3–5% and 15% of the control value for dry and humid conditions, respectively. This is considerably less than the reduction of DGEBA monomer content

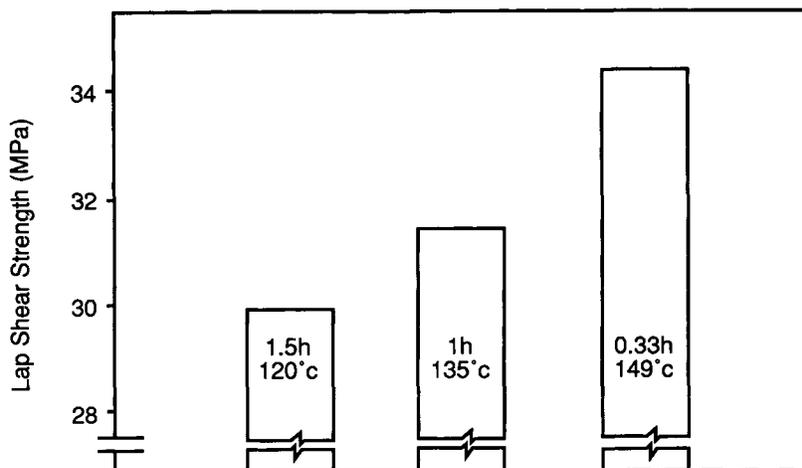


Figure 5 The effect of cure temperature on lap shear strength after a chromic acid pretreatment.

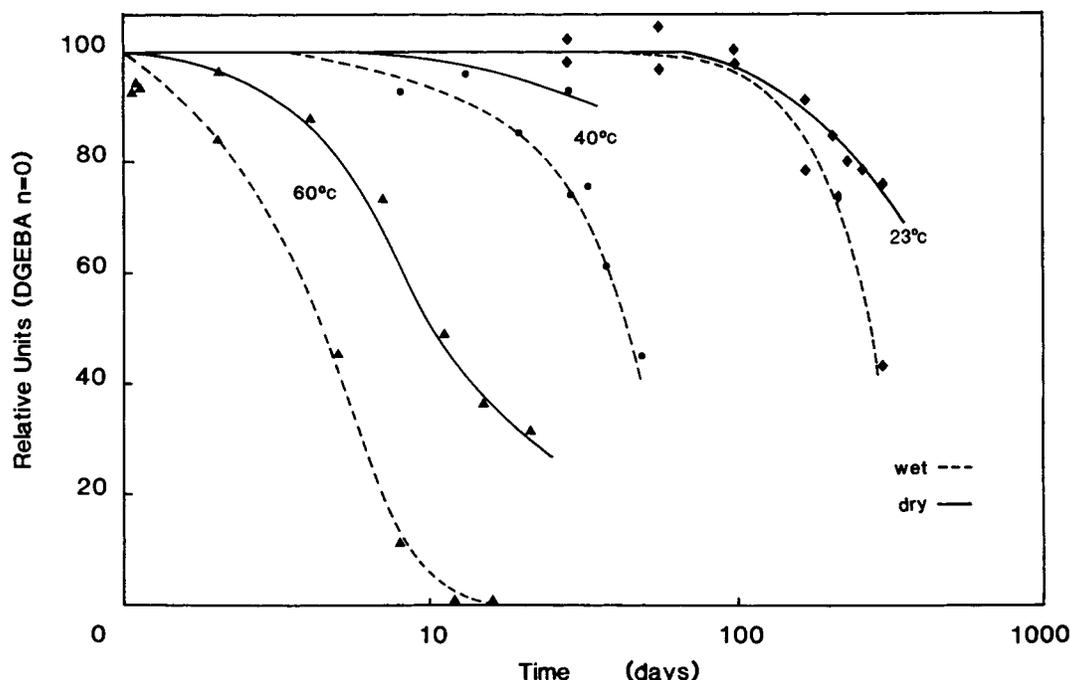


Figure 6 Depletion of monomeric DGEBA as a function of aging time, at various temperatures under both wet and dry conditions.

but in the same ratio. The difference arises because only one of the two epoxide groups is removed during reaction of the difunctional monomeric DGEBA. After 20 days, the (extrapolated end of) T_g for the dry aged material had increased by 10°C from the control value of 19°C and that of the wet aged material slightly more. At 60°C, the heat of cure had been halved in 6 and 20 days for wet and dry aging, respectively, and in the latter, the T_g had risen to 70°C; again depletion of monomer was more rapid (ca. 4 and 10 days, respectively, for 50% reduction). After 3 wet weeks at 60°C, more than 90% of the epoxide content had been reacted and the T_g of the adhesive had reached 90°C. The scatter in the heat of cure of the samples aged at 40°C was greater than would normally be expected, perhaps as a result of induction period variation and/or inhomogeneity in the small DSC samples, but at 60°C, the changes in heat of cure are proportionately greater and it can be seen (Fig. 7) that the aging is almost linear.

The DSC reaction profiles of the aging adhesive were not appreciably changed from those of the control material, and the T_g of the DSC cured sample was also unaffected (except in very aged wet samples where there was a slight lowering of the T_g). There was no melting endotherm near 210°C that would indicate the presence of unreacted dicy and, thus, no different cure mechanisms as found by Schneider et al. in similar systems.¹⁶

When compared with the three modified epoxy films (also of service temperature range -55 to 120°C) reported previously,^{4,5} where shelf lives of a few hours⁴ and about 50 days at 23°C and < 50% RH and about 8 days at 40°C under both wet and dry conditions⁵ were obtained, it is clear that the current adhesive is significantly more stable prior to cure, particularly in low humidity. In a damp atmosphere at the higher storage temperatures, the shelf life is drastically reduced, and as we have sug-

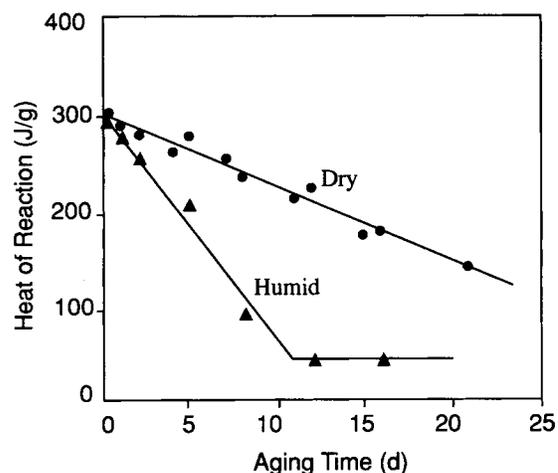


Figure 7 Heat of reaction by DSC after aging at 60°C under wet and dry conditions.

gested previously,⁵ the major reaction is probably that of advancement by the DGEBA resin and urea accelerator, a reaction that is accelerated by the presence of water.

Durability

Adhesive bond durability was assessed in terms of crack propagation resistance during exposure to a hostile environment (50°C and 96% RH) using the Boeing wedge test. This highly sensitive test, which simulates forces and effects at the metal–adhesive interface, is only qualitative since the initial crack length, and, hence, initial joint stress, is determined by the fracture toughness of the particular adhesive. Thus, a comparison of the crack propagation rates of different adhesive systems must be treated with caution. However, for any particular adhesive system, regardless of adherend surface pretreatment, the initial crack length remains fairly constant if cohesive (within the adhesive) failure occurs and significant comparisons can be achieved.

Figure 8 shows a comparison of crack propagation rates obtained from bonded aluminum wedge specimens prepared using chromic acid etch, epoxy silane, and sandblast-only pretreatments, respectively, and cured at various temperatures at 0.17 MPa pressure. Results clearly indicate that at all cure temperatures only the silane pretreatment confers good durability as judged by this test.

The poor performance obtained after only sandblasting the adherend was not surprising since there is much evidence to suggest that chemical surface pretreatments are essential to ensure the generation of stable oxide layers that interact with the adhesive to produce strong, hydrolytically stable, interfacial forces.¹⁷

Chromic acid etching is used extensively by the aircraft industry to prepare aluminum surfaces for bonding and is almost without exception the recommended adherend cleaning procedure specified in adhesive manufacturer's data sheets. However, previous studies have shown that the use of fresh chromic acid may lead to poor or variable bond durability, and improvements may be achieved through a "seeding" procedure¹⁸ in which traces of bare aluminum alloy, copper sulfate, or aluminum sulfate are added in order to "age" the solution. With the current adhesive, wedge tests using copper sulfate-modified chromic acid-etch pretreatment did not show any real improvement in crack propagation rates after curing at both 135 and 149°C under pressure of both 0.17 and 0.28 MPa. It must therefore be concluded that chromic acid-etched aluminum surfaces, although excellent for initial adhesion, may not provide long-term durability.

The effectiveness of the epoxy silane is of particular interest since this form of treatment is relatively simple and nontoxic and, thus, highly convenient for use in locations remote from ideal workshop

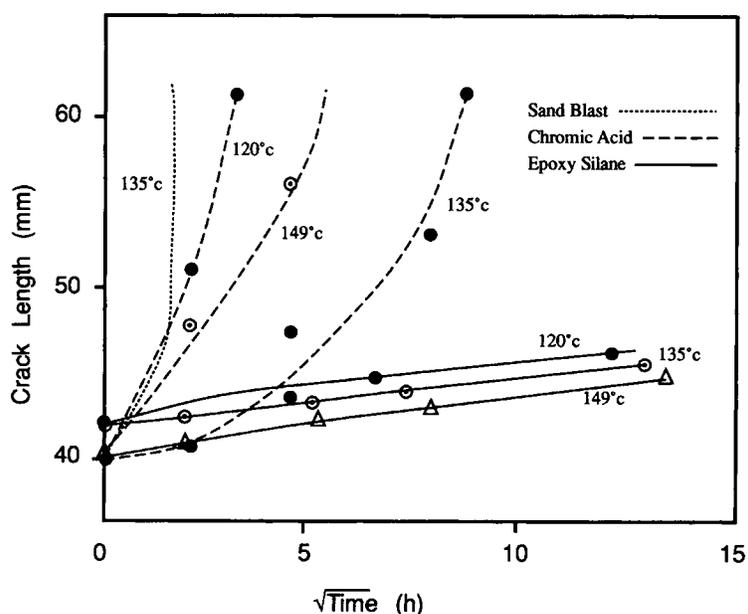


Figure 8 Wedge specimen crack propagation rates after various surface pretreatments and cure temperatures.

conditions or when carrying out *in situ* bonded aircraft repairs.

SUMMARY

1. The film adhesive was found to be a variant of the 120°C curing nitrile-epoxy systems using a urea-accelerated dicyandiamide cure. Two novel features were noted: the presence of bisphenol S and an almost insoluble urea, 1,1'-*p*-phenylene-bis(3,3-dimethyl) urea.
2. There are good reasons to believe that the improved stability can be explained by the reduced solubility of the urea accelerator, which, at the cure temperature, has very similar reactivity to the ureas used in this type of adhesive.
3. Full cure is obtained at 135°C, but only 90% reaction occurs at 120°C before vitrification.
4. Adhesive strength and durability are quite sensitive to aluminum surface preparation. As judged by the Boeing wedge test, a simple silane pretreatment confers excellent durability, a result that cannot be matched using chromic acid etching.
5. Its relatively high strength at elevated temperatures can be related to the comparatively high T_g of 155°C resulting from the addition of bisphenol S.
6. A shelf life of at least 3 months at 23°C can be expected in both wet and dry atmospheres for adhesives of this type of composition, but at higher temperatures, the adhesive is less stable, particularly under humid conditions.

The authors are indebted to the late Dr. Alan Moritz for the mass spectroscopy, Mr. Richard Davidson for the infrared analysis, and Ms. Frances Tolan and Mr. Tony Camilleri for providing technical assistance.

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Received January 7, 1992

Accepted April 10, 1992