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## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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**To cite this Article** Pearce, P. J. , Ennis, B. C. , Grabovac, I. and Morris, C. E. M.(1994) 'Off-Optimum Cure of Aerospace Epoxy Adhesives', *The Journal of Adhesion*, 47: 1, 123 – 132

**To link to this Article:** DOI: 10.1080/00218469408027094

**URL:** <http://dx.doi.org/10.1080/00218469408027094>

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# Off-Optimum Cure of Aerospace Epoxy Adhesives\*

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*(Received May 3, 1993; in final form August 7, 1993)*

Four epoxy film adhesives used in aircraft manufacture and repair have been examined to establish the effect of deviation from the cure cycle specified by the manufacturer. In addition to the variation of the cure cycle, two surface preparations of the aluminium adherends (chromic acid etch or grit blast followed by silane treatment) were evaluated. Thermal analysis was used to examine the cure envelope of the adhesive, and its extent of cure and glass transition temperature. The adhesive properties were assessed by shear strength (in both single lap joints and in Iosipescu configuration), durability (Boeing wedge test) and chemical resistance to selected aggressive fluids. The sensitivity of the performance of a particular adhesive to off-optimum cure conditions depends on its composition and needs to be determined, not predicted.

**KEY WORDS** aerospace film adhesives; surface preparation; cure conditions; shear strength; durability; thermal analysis.

## INTRODUCTION

Structural adhesive bonding is now extensively used in the construction and repair of both civil and military aircraft. Most of these adhesives comprise epoxy-based formulations with resin and hardener combined to form a film which requires the combination of heat and pressure for effective cure. The combination of both reactants imposes considerable restriction on the choice of hardener, otherwise the physico-chemical description of cure of these thermoset epoxy formulations is unexceptional.<sup>1,2</sup>

However, practical considerations dictate two common cure cycles—1 hour at either 250°F or 350°F (121°C or 177°C). The manufacturers' data sheets seldom provide guidance on the effect of departure from the recommended cure condition(s). Because there is a considerable variation between contending formulations, the response of these materials to what might be termed "off-optimum cure" is a matter of some interest since the actual conditions which pertain to a specific application (particularly a repair) may diverge quite markedly from the

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\*Presented at the Sixteenth Annual Meeting of The Adhesive Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

recommended conditions. When this happens it is important to have some knowledge of how the adhesive (either pristine or aged) will respond.

The present report is directed to the broader picture of off-optimum cure of four film adhesives used in Royal Australian Air Force aircraft. Apart from composition analysis of the materials, the cure cycles were explored by thermal analysis and the adhesive shear strengths investigated *via* single overlap joints and by the Iosipescu test configuration (a potentially superior indicator of the bulk shear properties of adhesive in a joint).<sup>3</sup> Response to surface treatment of the aluminium adherends and glass transition temperature ( $T_g$ ) have been examined. Resistance to a number of aggressive fluids commonly encountered in aircraft operations has also been assessed. The emphasis is on the general approach to the potential problem, rather than specific detail for particular techniques (which are referenced) or adhesives.

## EXPERIMENTAL

All adhesives were stored at  $-18^\circ\text{C}$  until required.

### Compositional Analysis

The composition of the four film adhesives used in this study was determined by a combination of high precision liquid chromatography (HPLC) and infrared spectroscopy (IR). Detailed procedures are described elsewhere.<sup>4</sup>

### Thermal Analysis

A Dupont Thermal Analyst 2000 with 910 Differential Scanning Calorimetry (DSC) cell was used. Quantitative dynamic DSC curves were obtained at  $10^\circ\text{C}/\text{min}$  in air (although other heating rates were also used when studying the reactivity and latency of individual adhesives). Isothermal cure was achieved by dropping the sample into the preheated cell, and the  $T_g$  of the resultant cured material was determined by reheating the sample at  $10^\circ\text{C}/\text{min}$ ; because it is frequently difficult to identify the onset of the transition in these complex mixtures, the quoted temperature is the extrapolated end of the transition, which is readily identifiable and is convenient for comparative purposes.

### Mechanical Properties of Bonded Joints

Single lap joints were made and tested in accordance with ASTM D1002 using 2024 T3 aluminium alloy adherends. Two surface pretreatments were used: (a) a degrease in a trichloroethane vapour degreaser followed by a chromic acid etch (10 min at  $65\pm 2^\circ\text{C}$ ; bath composition, 375 g  $\text{H}_2\text{O}$  + 68 mL 98%  $\text{H}_2\text{SO}_4$  + 50 g  $\text{K}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) or (b) a degrease, then grit-blast followed by immersion in an aqueous solution (1% v/v) of glycidoxypropyltrimethoxysilane ( $\lambda$ -GPS, Dow Corning Z6040). A number of cure cycles were used, as summarised in Table I, using a heated platen press. The ultimate shear stress was also determined by the

Iosipescu method<sup>3</sup> using 5083 aluminium alloy adherends pretreated according to method (a) above.

TABLE I  
Cure cycles used for the preparation of bonded joints

Adhesive	Cure cycle		
	1	2	3
A	1 hr/177°C*	2 hr/132°C	—
B	1 hr/177°C*	2 hr/132°C**	5 hr/132°C
C	1 hr/177°C*	3 hr/150°C	2 hr/150°C
D	1 hr/121°C*	15 hr/80°C	2 hr/100°C

\*Recommended by manufacturer

\*\*Aircraft manufacturer alternative

### Chemical Resistance

The resistance of bonded joints to a range of liquids commonly encountered in aircraft operations was assessed by immersion of lap shear joints, prepared as above, for 30 days in the liquids in question after which the lap shear strength was determined. The liquids were: salt water (about 3.5% NaCl), jet fuel (JP8), hydraulic oil (Mobil Aero HFE H515) and deicing fluid (85% ethylene glycol, 10% water, 5% isopropanol).

## RESULTS AND DISCUSSION

### Composition

The chemical composition and some selected thermal and mechanical properties of the four adhesives used in this study are shown in Table II. Adhesives A, B and C have a manufacturer's recommended cure cycle of 1 hour at 177°C and their relatively complex formulations contain a mixture of epoxy resins, including species with a functionality of 3 or greater in order to confer improved high temperature performance. A and B use diaminodiphenylsulfone (DDS) and dicyandiamide (Dicy), respectively, as curing agents; Adhesive C uses the unusual mixture of both curing agents. The presence of reactive rubber in the latter adhesive leads to a significant improvement in shear and peel strength but at the expense of  $T_g$ , which is about 50°C lower than the other two "177°C" curing systems. Adhesive D is a typical rubber-modified, DGEBA-based, urea cured, lower temperature film with excellent shear and peel strength, but fairly low  $T_g$  and, therefore, reduced service temperature.

All the curing agents are "latent" in that they are relatively unreactive at ambient temperature and need to be heated to induce reaction. Aspects of latency have been considered elsewhere.<sup>5,6</sup>

TABLE II  
Composition and selected properties of the adhesives

	A	B	C	D
Epoxy resins*	TGAP cresol novolac epoxy DGEBA	TGAP cresol novolac epoxy DGEBA	TGMDA DGEBA 4BrDGEBA	DGEBA
Curing agent**	DDS	Dicy	DDS Dicy	TDI-DMA
Modifier***	—	—	CTBN	CTBN
Other Additives	Kevlar filler glass support	Kevlar filler glass support	TiO <sub>2</sub> , dye polyester support	dye polyester support
Quoted Service Temperature (°C)	-55 to 232	-55 to 204	-55 to 149	-55 to 121
Max, T <sub>g</sub> (°C)	>200	>200	150	114
Typical Ambient Lap Shear Strength (MPa)	15.9	17.9	35.5	43.5
Typical T-Peel Strength (N/25.4mm)	<10	<10	50	172

\*TGAP, triglycidyl 4-amino phenol; DGEBA, diglycidyl ether of bisphenol A; TGMDA, tetraglycidyl methylene dianiline; 4BrDGEBA, diglycidyl ether of tetrabromobisphenol A.

\*\*DDS, 4,4'-diaminodiphenyl sulfone; Dicy, dicyandiamide; TDI-DMA, 2,4-toluenediisocyanate/dimethylamine adduct.

\*\*\*CTBN, carboxyl terminated butadiene-acrylo nitrile reactive rubber.

### Cure Temperature and Time

For each adhesive the cure was examined by DSC. The fresh adhesive was first heated at 10°C/min to give an indication of the reactivity to be expected. Typical curves are shown in Figure 1 from which it can be seen that the dynamic cure profiles show different onset temperatures and reaction ranges, even in adhesives of the same nominal class. More information on the adhesive cure profile was obtained when the sample was dropped into the preheated DSC cell and the cure reaction followed to completion. An overview (Figure 2) of these isothermal studies compares the four adhesives giving the time to complete reaction at various temperatures. However, it is most important to recall that in thermosetting systems the extent of reaction at a particular temperature may be limited by vitrification and that if such a vitrified system is heated to a higher temperature, further reaction may occur. Thus, while Figure 2 shows the time to complete reaction at different temperatures, the extent of reaction at a particular temperature may be quite different. For example, for Adhesive B complete reaction at 130°C entails about 25% less reaction than complete reaction at 177°C. This effect is shown in Figures 3 and 4 which give the DSC curves of samples that have been cured isothermally in the DSC cell at temperatures close to those recommended by the manufacturers and at substantially lower temperatures, respectively. (In this context it should be pointed out that the temperature profile during isothermal cure

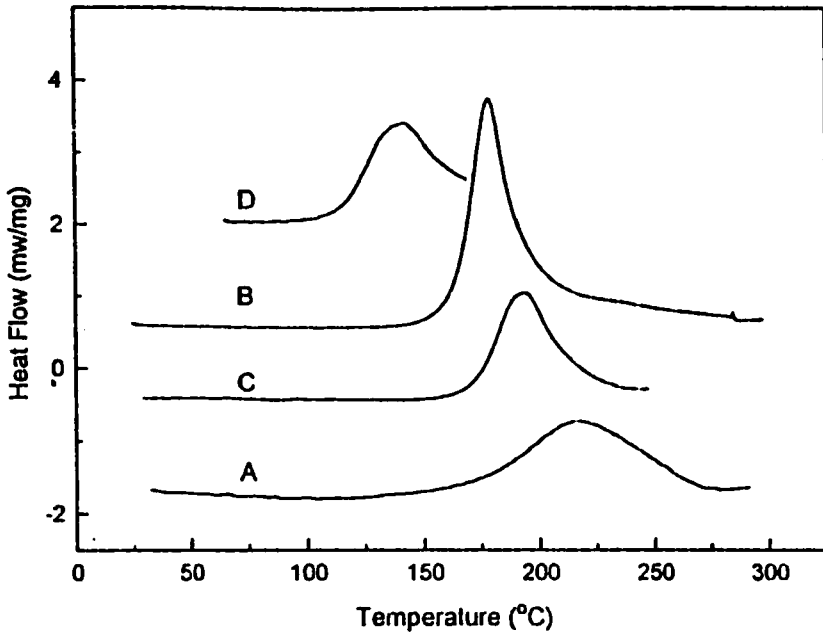


FIGURE 1 DSC curves of fresh adhesives; Adhesive D was heated at 5°C/min instead of 10°C/min. The curves are arbitrarily displaced vertically.

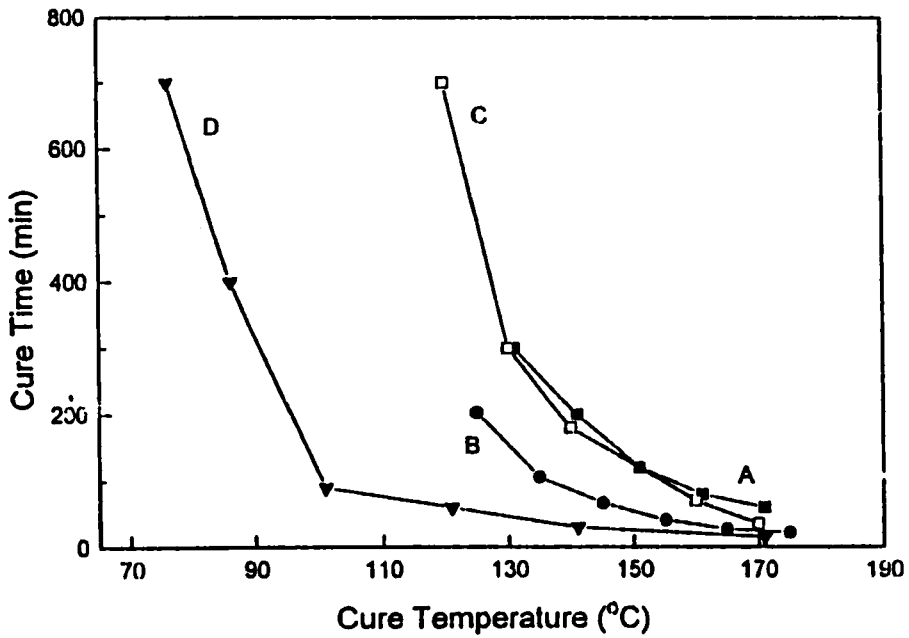


FIGURE 2 The time needed for the various adhesives to complete detectable cure (by isothermal DSC) at different temperatures.

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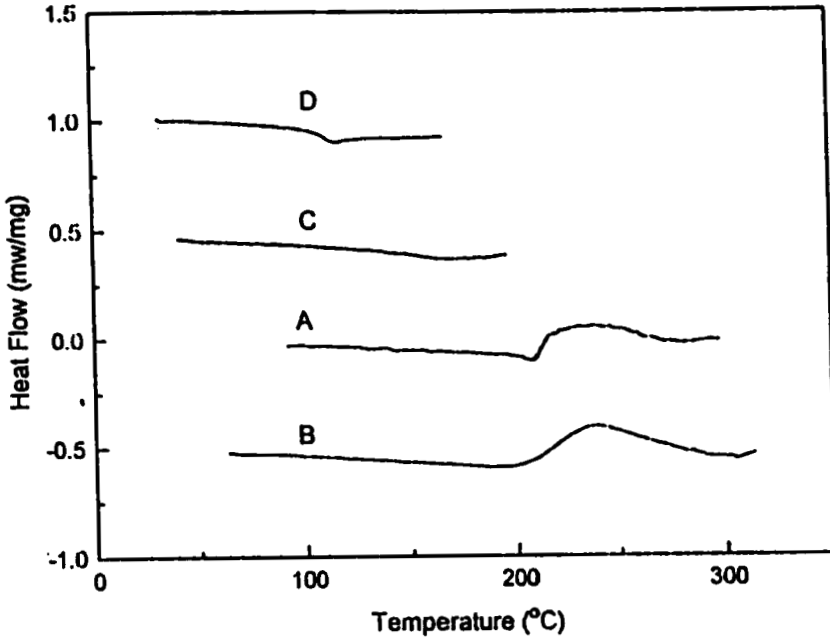


FIGURE 3 DSC curves of the adhesives after the recommended cure in the DSC cell (cycle 1 temperature [see Table I], isothermal).

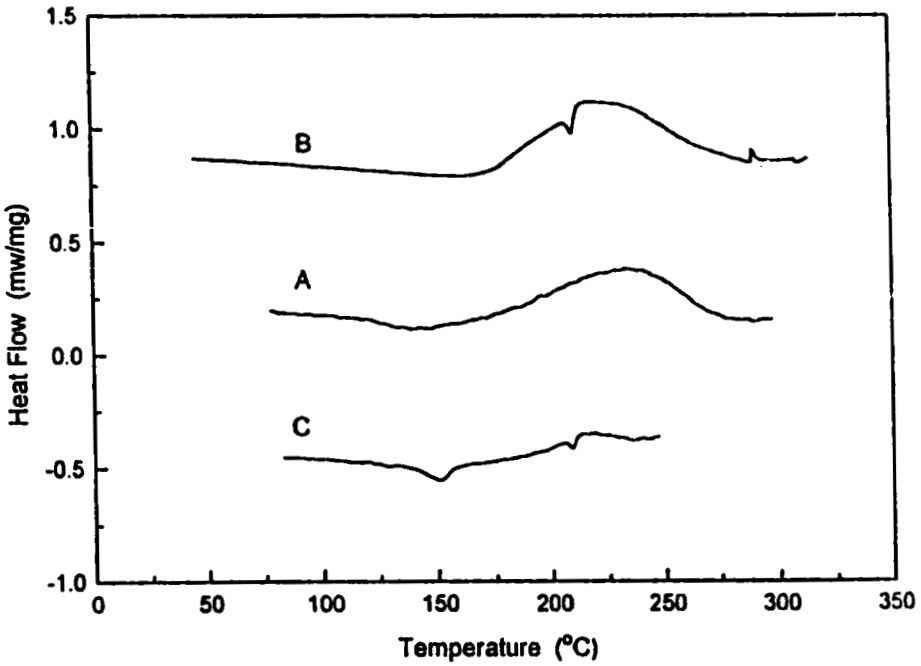


FIGURE 4 DSC curves after non-standard cure in the DSC cell: Adhesive A, 15h/120°C; Adhesive B, 2h/130°C; Adhesive C, 15h/120°C.

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in a DSC cell is substantially different from that which will be experienced in practice and that this can affect the final outcome as shown in the detailed comment, below, on Adhesive D. The application of pressure is less likely to affect the cure, but restraint of volatiles could have an influence.) The glass transition temperatures and any residual heat of reaction can be obtained when the isothermal samples are reheated.

A summary of the cure temperature-time studies for each of the four systems is given below.

*Adhesive A* DSC curves at constant heating rate show that reaction is quite appreciable from below 100°C (at 2.5°C/min) and that the rate of reaction slowly increases to peak at 182°C (at the same heating rate). Even at this slow heating rate reaction continues to over 250°C, and for material fully cured at 177°C there is some residual reactivity in the temperature range 190–280°C. During isothermal DSC cure the heat of reaction changes by less than 10% between 130 and 170°C and more than 85% of the 177°C achievable cure is reached within 5 hours at 130°C. There are some difficulties in both these measurements since there is some reaction which is not measured during the heating to isothermal temperature, and the residual reaction may involve some reaction not normally involved in the cure. The  $T_g$  of materials cured in this manner is not a particularly meaningful measurement because of the ongoing reaction. All show considerable endotherms attributable to physical aging some 40°C above the isothermal cure temperature.

*Adhesive B* This adhesive, like Adhesive A, does not react completely at the recommended cure temperature but, in contrast, the reaction does not proceed as readily at lower temperatures. This doubtless reflects the reactivity of the primary amine moiety of DDS in Adhesive A which is absent from Adhesive B. The residual reactivity steadily increases as the temperature is lowered and at 130°C there appears to be about 20–25% less reaction than at 177°C. As with Adhesive A, residual reactivity negates meaningful measurement of  $T_g$ .

*Adhesive C* When heated at 10°C/min this system shows appreciable reaction above about 140°C, with maximum rate at 193°C and effectively complete reaction by 250°C; at 5°C/min reaction occurs slightly earlier and is complete at 230°C after maximum rate at 183°C. It is reasonable to assume that the maximum rate coincides with gelation and, consequently, under the normal cure schedule the adhesive should be gelled by the time the cure temperature is reached.

From the time to complete the cure at various temperatures given in Figure 2 it can be seen that the reaction time is short at the recommended 177°C (about 20 mins), but excessively long below 130°C. It is significant that, even at 120°C, there is approximately 70% cure after 5 hours, and after 15 hours the residual reactivity is scarcely measurable.

The DSC curves of the materials that have been isothermally cured (to completion) show that the end of  $T_g$  is 160 to 165°C, with only slightly lower values for material cured at lower temperatures. One difference that is seen after low temperature cure (140°C or lower) is the persistence of an endotherm due to Dicy melting. The significance of this is not obvious.



*Adhesive D* This adhesive was found to be tolerant of cure conditions and the manufacturer's statement that cure conditions may be varied over the temperature range 93°C to 177°C was generally confirmed. It has been found that complete reaction can be achieved in 10 hours at temperatures as low as 80°C. It was found that the  $T_g$  of the cured material was determined by the curing temperature and peaked at a cure temperature of 100°C ( $T_g$  114°C). Material cured at higher temperatures had substantially lower  $T_g$  (93°C after cure at 141°C). While further heating at 120°C raised the  $T_g$  (to 114°C) of the low temperature (below 100°C) cured materials, the higher temperature cured materials were not affected. This behaviour is unusual, but not unique,<sup>7</sup> and in apparent contradiction of the time and temperature equivalence underlying the construction of Time Temperature Transformation (TTT) diagrams proposed by Gillham (see, for example, Prime<sup>8</sup>). The most probable explanation is that the competitive reactions possible in complex mixtures, and therefore the mix of product (and reactive intermediate) structures, have different kinetic parameters (temperature dependence).

For most adhesives, platen-press-cured and DSC-cured samples have the same  $T_g$ , but when this adhesive was cured at temperatures above 100°C press cured samples had a higher  $T_g$  because of the longer time at lower temperatures while the press was ramped to cure temperature.

### Performance of Bonded Joints

The shear strength of lap joints, given in Figure 5, shows the effect of different cure cycles and surface pretreatments on adhesive performance. For the higher temperature systems (A & B) the lower temperature cure (cycle 2) resulted in a reduced shear strength on both surface pretreatments, especially for Adhesive A. This is also seen for Adhesive D, but to a lesser extent. For Adhesive A and B the silane surface treatment gave a lower shear strength than the chromic etch pretreatment. Adhesive D was similar, but not as sensitive, and Adhesive C was quite tolerant of this range of bonding conditions.

That the lower cure temperature is disadvantageous for the bond strength of Adhesives A and B is not surprising since, from Figure 2, it is evident that 2 hours at 132°C is inadequate for Adhesive A and barely sufficient for complete reaction of Adhesive B. In addition, "complete reaction" at 132°C for Adhesive A leaves at least 15% residual reactivity, while for Adhesive B the figure is 20–25%. On the other hand Figure 1 indicates that for Adhesive C, 3 hours at 150°C is a suitable alternative to 1 hour at 177°C on the basis of completeness of reaction.

These results were supported by preliminary Iosipescu shear strength values *vs.* lower temperature cure schedules (Figure 6) obtained using chromic-acid-etched 5083 aluminium blocks (there was not suitable stock of the 2024 T3 used in the lap joints); this test configuration minimises peel forces and adherend deformation during the test. Adhesive B, cured for 2 hours at 132°C, gave markedly inferior shear strength joints, compared with 1 hour at 177°C, while 5 hours at 132°C resulted in joints of intermediate strength, *i.e.* allowing sufficient time at the lower cure temperature for the adhesive to react as much as possible at that temperature minimises the ultimate strength penalty. Adhesive D gave similar Iosipescu shear strength values for each of the three cure cycles used.

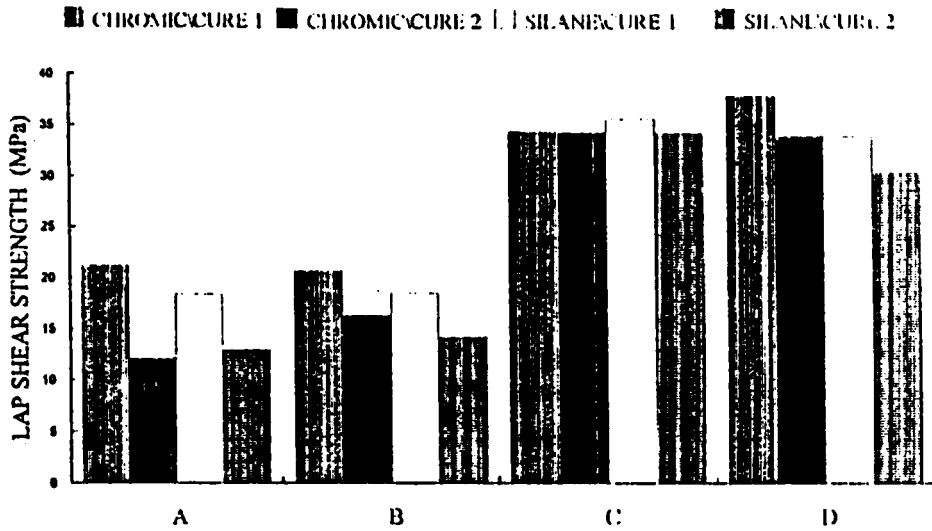


FIGURE 5 The effect of cure cycle and surface preparation on the shear strength of bonded lap joints.

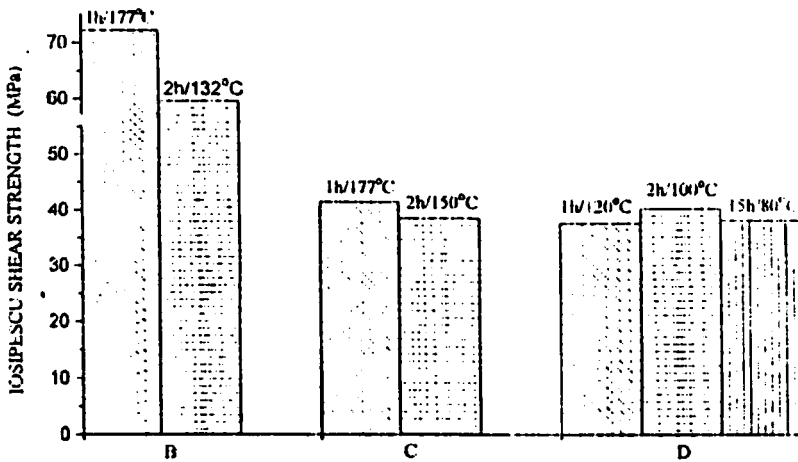


FIGURE 6 The effect of lower cure temperature on the Isoipescu shear strength of selected adhesives.

**Chemical Resistance**

Lap shear strength of joints, made under the same conditions as in Figure 5 and determined after 30 days immersion in the various fluids, showed only very minor changes from the unexposed controls. Inadequately cured specimens (as discussed above) showed no greater susceptibility to the influence of the fluids than those more adequately reacted.

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## CONCLUSIONS

In general, a reduced extent of adhesive cure reaction can be expected to have a deleterious effect on joint performance. Frequently, it is during the last few per cent of the reaction that the crosslink density is enhanced significantly and the  $T_g$  is raised; coincidentally, the concentration of reactive entities is reduced, thereby minimising the likelihood of further reaction leading to changing properties during service. Further, in the cure of complex mixtures such as most epoxy adhesives (which may consist of a number of types of epoxy resins of different reactivities with one or more curing agents), "the cure reaction" is in fact a smorgasbord of reactions such that different cure conditions can be expected to result in different chemical structures. These complexities are obscured by classifying most aircraft adhesives as being either a 121° or a 177°C curing system!

The present work has demonstrated the different responses to cure temperature for four adhesive formulations which differ significantly in composition and in location of the recommended cycle in the possible cycle window. It should be kept in mind that for *in situ* bonded aircraft repairs, safety margins are needed to accommodate the fact that part of the repair area may fail to reach the nominal cure temperature because of adjacent heat sinks. An attempt has been made to assess the adequacy of suggested "equivalent" cure schedules in terms of such factors as ultimate shear strength and chemical resistance. Other factors, such as creep under sustained load and fatigue, should also be considered before a final judgement on alternative cure cycles is made. What is evident is that the response to "off-optimum" cure conditions is dependent on the adhesive composition.

## Acknowledgements

The authors gratefully acknowledge the infrared analytical work conducted by R. G. Davidson and the technical assistance provided by G. Simpson and A. W. Camilleri.

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