JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 1431–1440 (1976)

The Effect of State of Cure on Bond Performance For an Epoxy Resin System

C. L. BRETT, *Materials Quality Assurance Directorate, Royal Arsenal East, Woolwich, London, SE18 6TD, England*

Synopsis

A study of the influence of the state and mode of cure of an epoxy resin, diglycidyl ether of bisphenol A cured with 4,4′-diaminodiphenylmethane, has been made. The state of cure was assessed by differential scanning calorimetry as residual heat of reaction and a transition temperature T^* corresponding to either the melting point or the glass transition temperature. The state of cure was varied by controlling both the time and temperature of cure. Bond strengths can be related to either T_g or residual heat of reaction, but the different cure schedules produce different relations; simultaneous measurement of both parameters is necessary to specify the state of cure. Some additional work has been carried out on the effect of delayed cure on bond performance and on the effect of varying the cure schedule for a phenol-formaldehyde adhesive. Both single- and double-overlap joints have been used and a constant single/double bond strength ratio has been found. This constant is different for the two adhesives, reflecting their different behavior in shear.

INTRODUCTION

This research was intended to provide a better knowledge of how changes in the state of cure of an adhesive affect the performance of the adhesive. The system chosen for this study was a typical unmodified epoxy resin, Ciba Geigy (U.K.) Ltd. resin AY 105 (diglycidyl ether of bisphenol A) cured with HT 972 (4,4′-diaminodiphenylmethane).

The cure of epoxy resins has been studied by differential scanning calorimetry (DSC) by Fava,[1] Campbell and Worsdall,[2,3] and Barton.[4] This technique gives a quantitative measurement of the residual amount of reaction and also allows determination of the glass–rubber transition temperature (T_g). Both quantities can be used to characterise the state of cure of a resin, but, as Barton found, measurement of the residual heat of reaction becomes more difficult as the reaction nears completion and the T_g becomes a more meaningful characterization of the state of cure.

EXPERIMENTAL

Differential Scanning Calorimetry

A Perkin-Elmer differential scanning calorimeter DSC 1B was used. This is a more sensitive version of the DSC 1 model. The instrument can be operated

Copyright © Controller HMSO, London, 1975
Published by John Wiley & Sons, Inc., 1976

isothermally or on a temperature program at 0.5–64°C/min. The calorimeter is calibrated from the latent heat of fusion of pure indium (6.8 cal/g) and the temperature programmer from the melting points of the following compounds: *n*-octane (−56°C), ice (0°C), 8-hydroxyquinoline (74°C), acetanilide (114°C), and indium (156°C).

In all cases, samples were taken from the fillets of adhesive at the ends of the joints. Of the six joints assembled for each set of conditions, one had a deliberately large fillet; this was subjected to essentially the same thermal history as the adhesive inside the joint. Joints with large fillets were indistinguishable, in terms of bond strength, from joints with normal fillets and provided sufficient material for the DSC (ca. 10-mg samples).

The scanning procedure was essentially the same as that used by Campbell and Worsdall[2,3]: the sample, in a sealed capsule, was placed in the calorimeter cell, equilibrated at 30°C, and then scanned at 16°C/min from 30° to 250°C.

The cure of an epoxy resin is an exothermic process, and the heat evolved can be detected quantitatively by the DSC, thus giving a measurement of the amount of reaction remaining in the sample. When the sample is grossly undercured, an endotherm, corresponding to sample melting, is observed prior to the exotherm. In such cases, no T_g is observable and the temperature at which melting occurs is recorded instead. At advanced states of cure, a distinct T_g is observable but the exotherm then becomes very small and cannot be accurately assessed for this resin system. In this paper, the symbol T^* is used to refer to either the melting point or the glass transition temperature as appropriate to the sample. The transition temperature is subject to smaller errors than the heat of reaction since it is a simple temperature measurement independent of sample size, whereas the heat of reaction is obtained from the area between two curves, viz., the sample exotherm and an assumed baseline. This area is measured with a planimeter and compared with the calibration curves.

Joint Assembly

Both single- and double-overlap joints were used in this study. The single overlaps were assembled from 16 SWG aluminum-clad alloy to BS 2L73 to give a half-inch overlap, one inch wide. The double overlaps (tuning fork configuration) were assembled from two strips of 16 SWG alloy and a central strip of 8 SWG alloy with the same overlap as for the single lap joints. All surfaces were pickled in chromic/sulfuric acid as described in Def Stan 03-2/1.

Isochronous Cure

For these experiments, the joints were assembled in dead load jigs which were placed in an air-circulating oven at the required temperature for 24 hr. In the case of double-overlap joints, good linearity could only be maintained by assembling one joint per jig. The joints were cured under 35 kN/m^2 pressure.

Isothermal Cure

For these experiments, the joints were first assembled in a cold jig, the joints being held together by masking tape to allow subsequent handling. They were

then transferred to jigs which had already been heated to the required temperature (one joint per jig). Under these conditions, the joint was heated rapidly to its curing temperature (experiments indicated a rise time of ca. 3 min). Cure was terminated after the required time by removing the joint from the hot jig and placing it in a cold jig. Cure time was thus controlled to ± 5 min.

Joint Testing

This was carried out on an Instron Universal testing machine. Single-lap joints were strained at 0.5 mm/min and double laps, at 1 mm/min to give similar loading rates. Normally five to six joints were tested and the average bond strength obtained. Joints were tested ca. 24 hr after completion of the curing schedule.

Examination of Broken Joints

A number of techniques were used in examining the broken joints; two of these (iodine staining and use of polarized light) are new and have been reported elsewhere.[5]

The adhesive system used in this study reacts with iodine dissolved in trichloroethylene/ethanol to give an intense blue-green stain. The color is confined to the outer 5–10 μm layer and renders even thin films of resin easily visible.

The use of polarized light provides a useful means of detecting thin films of resin on the metal surface.

A copper-plating technique based on a method used by Jennings[6] was also employed. Fehlings solutions A and B (A = 34.64 g/dm^3 $CuSO_4 \cdot 5H_2O$, B = 60 g/dm^3 sodium potassium tartrate) were made up and mixed in equal volumes prior to use; the resulting solution was then diluted by a factor of two. Plating was achieved by immersion of the aluminum-clad test piece into this solution at room temperature. Plating remains selective if the test piece is withdrawn and washed after ca. 8–10 sec, i.e., when darkening of the metallic surface is apparent but before the reagent has penetrated any thin organic layers on the surface (only the etched surface of the joint is plated). This technique has a wider range of applications than the iodine stain.

The action of sodium hydroxide solution on these surfaces has been studied using low power optical microscopy. From these studies, it is evident that the reagent penetrates cracks in the film and attacks the underlying surface causing detachment of the film. This explains the need for short immersion times when using the Fehlings solution for copper plating.

Both optical and scanning electron microscopes were used to examine the fractured surface. These instruments are of limited value since only small areas can conveniently be examined. The scanning electron microscope, in the x-ray emission microprobe mode, was of value in distinguishing areas of resin stained with iodine and areas of bare metal. Use of the microscope in this mode is also of value for the examination of copper-plated test pieces. The electron beam can penetrate thin layers of resin to give aluminum x-ray emission. Copper plating only occurs on areas of bare metal, and hence copper x-ray emission cannot arise from areas covered with adhesive.

RESULTS

Isochronous Cure

Table I shows the results obtained for residual heat of reaction (duplicate samples) and T^* for joints cured at various temperatures for 24 hr together with bond strengths for single- and double-lap joints. From these results, it is evident

TABLE I
Isochronous Data. Effect of Cure Temperature on Residual Heat of Reaction, T^*, and Bond Strength

Cure temp., °C	Residual heat of reaction, cal/g		T^*, °C	Bond strength, kN	
	Individual	Mean		Single lap	Double lap
50	21.7, 19.5	20.6	78.5 ± 2	1.95 ± .3	7.75 ± .5
58	13.0, 16.3	14.6	85.5 ± 2	4.85 ± .2	20.7 ± 2.0
72	8.7, 10.4	9.5	99.5 ± 2	9.3 ± .2	32.5 ± .2
80	2.9, 3.1	3.0	97 ± 2	9.5 ± .2	32.5 ± .2
50[a]	12.4, 16.4	14.4	77 ± 2	—	5.72
60[a]	6.8, 8.7	7.7	85 ± 2	—	22.7
68[a]	5.3, 7.3	6.3	99 ± 2	—	33.2

[a] Earlier experiments with the same batch of resin but different batch of hardener.

that both T^* and the residual heat of reaction measure the state of cure of the resin with similar accuracy. Figure 1 shows the relationship between bond strength and residual heat of reaction; Figure 2 relates bond strength to T^*. The observed relation between T^* and bond strength is similar to that found by Cassidy et al.[7] who used a range of additives to vary the T_g of an epoxy resin.

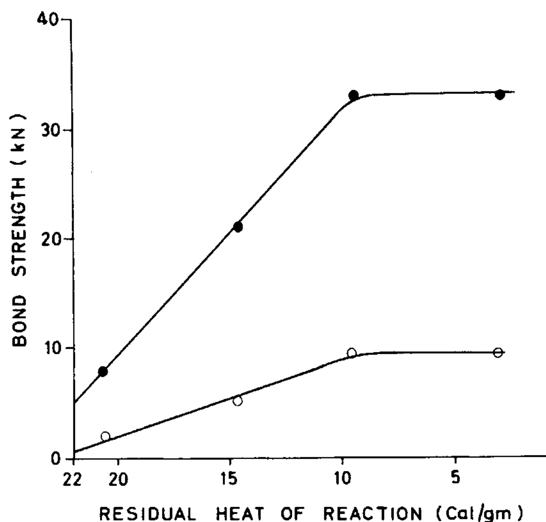


Fig. 1. Isochronous cure—variation of bond strength with residual heat of reaction: (O) single laps; (●) double laps.

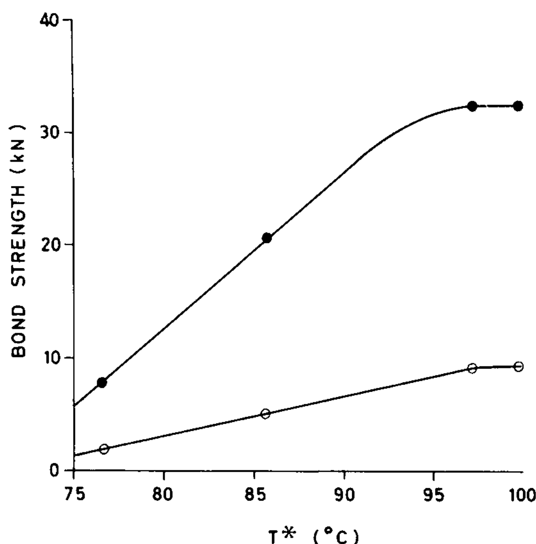


Fig. 2. Isochronous cure—variation of bond strength with T^*: (○) single laps; (●) double laps.

TABLE II
Relationship Between Cure Time at 81°C, Residual Heat of Reaction, T^*, and Bond Strength

Cure time, hrs	Residual heat of reaction, cal/g		T^*, °C	Bond strength, kN	
	Individual	Mean		Single lap	Double lap
1.16	22.0, 26.6	24.3	49 ± 2	0.7 ± .07	3.1 ± .6
1.33	22.7, 23.6	23.1	55.5 ± 2	1.4 ± .3	5.4 ± .7
1.5	10.7, 14.5	12.6	65.5 ± 5	6.8 ± .4	21.4 ± 5
2.0	8.6, 12.4	10.5	86 ± 2	—	32.9 ± .2
3.0	2.9, 3.1	3.0	97 ± 2	9.5 ± .1	32.5 ± .2

Isothermal Cure

Table II shows the relationship between the cure time at 81°C, the residual heat of reaction, T^*, and bond strength. Figures 3 and 4 illustrate the relationship indicated in Table II, viz., bond strength versus heat of reaction and bond strength versus T^*.

Mode of Joint Failure

For single-lap joints having a low fractional cure (ca. 70%), the iodine staining technique indicated that the failure had occurred in the resin very close to one adherend surface. The evidence for this was that a uniform light blue-green stain could be formed over the entire joint area on one adherend. Sectioning a piece of stained resin had shown[5] that the maximum depth of penetration was 50 μm for heavy staining, and the lightness of the stain for these test pieces suggested that the film thickness was ca. 5 μm or less (cf. glueline thickness ca. 0.001 in. ≡

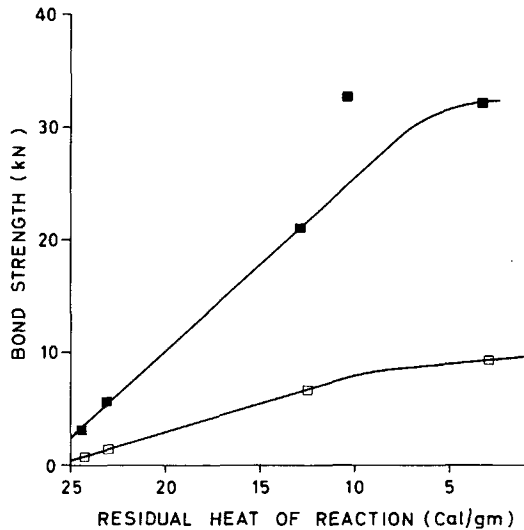


Fig. 3. Isothermal cure—variation of bond strength with residual heat of reactions: (□) single laps; (■) double laps.

25 μm). This conclusion was supported by the observation of interference colors with the aid of polarized light.

The thin films of resin on broken joints of low cure often displayed a curious ridge pattern. This may be attributed to stepwise crack propagation at approximately equal strain energy increments. Similar behavior has been observed directly using Perspex adherends where the intermittent crack growth was clearly visible (cf. also ref. 8).

For higher fractional cures (ca. 85%), the crack propagated through the center of the bond leaving approximately equal amounts of adhesive on each half of the joint.

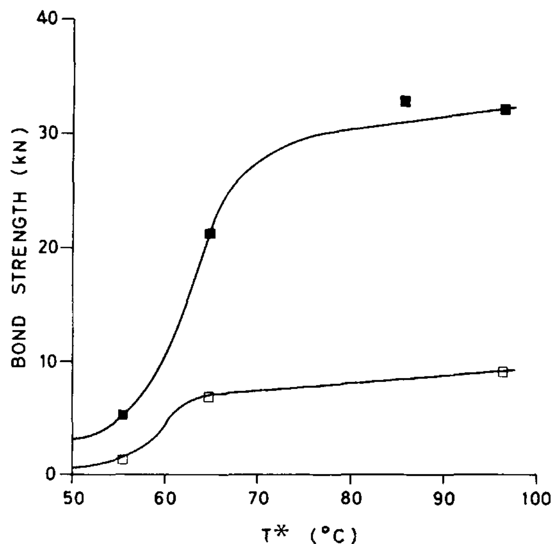


Fig. 4. Isothermal cure—variation of bond strength with T^*: (□) single laps; (■) double laps.

At the highest fractional cures used (90–95%), failure was no longer cohesive. Both adherends had irregular patches of adhesive, particularly at the ends of the adherends, and patches of "bare" metal corresponding to the patches of adhesive on the other half of the joint. The presence of "bare" metal indicated that failure had been at (1) the interface, (2) in the oxide layer, (3) in the metal, or (4) in the adhesive but very close to the surface. The results of iodine staining and copper plating both eliminated (4). Dipping a freshly broken joint (within 10 sec) in mercury indicated that (3) did occur but was rare. (A fresh aluminum surface quickly forms an amalgam which reacts readily with oxygen.) It was not possible with the techniques available to distinguish between (1) and (2). Auger spectroscopy would indicate the presence or absence of alumina on the adhesive and the presence or absence of an organic layer on the metal oxide surface.

Similar observations to the foregoing apply in the case of double overlaps. The chief differences were that the central adherend was normally left with a thin adhesive layer and that little "adhesive" failure was seen even at high fractional cure.

Effect of Delay Between Assembly and Cure

A number of joints were assembled and stored at 25°C for varying periods before being cured at 80°C for 3 hours. The results of this experiment are shown in Table III.

TABLE III
Effect of Storage Time (at 25°C), Prior to Cure at 80°C for 3 Hours, on Bond Strength (Single-Lap Joints)

Storage time, days	Bond strength after cure at 80°C for 3 hr, kN	Residual heat of reaction before final cure, cal/g
0	9.5 ± .1	88.8
1	7.7 ± .2	64.6
2	7.1 ± .6	33.0
3	4.8 ± .9	—
5	5.8 ± .8	—
14	5.6 ± .6	30.0

Partial cure of the viscous resin at 25°C probably produces a crosslinked structure which is sterically hindered from giving the normal crosslinking on subsequent cure at 80°C. These results emphasize the need to complete the entire bonding operation as quickly as possible.

Redux 775 RN

A few experiments were conducted using Redux 775 RN film (phenol-formaldehyde/poly(vinyl formal) on a nylon support). Joints were assembled in cold, spring-loaded jigs subjected to a pressure of 690 kN/m^2 and then placed in an oven at the required temperature for 1½ hr. Bond strength increased slightly with decreasing cure temperature in the range of 135–165°C. It is not possible to assess the state of cure of this adhesive by DSC because endothermic processes

TABLE IV
Effect of Cure Temperature on Bond Strengths for Redux 775 RN

Cure temperature °C	Bond strengths, kN	
	Single lap	Double lap
135	12.5 ± 0.2	30.6 ± .2
150	12.0 ± .15	30.0 ± 1.5
165	11.1 ± .15	29.4 ± .15

(emission of volatiles, etc.) mask the cure exotherm and the T_g. The results are shown in Table IV.

DISCUSSION

It may be noted that, in the case of the joints bonded with epoxy resin, the strength of a single-lap joint is a constant fraction (0.264 ± 0.026) of the strength of a double-lap joint in the same state of cure. The same observation is true for Redux 775 RN over the limited range of cure used; in this case, the constant ratio is 0.40. These observations are simply explained since failure is normally cohesive and the stress at failure is determined by the shear strength of the resin (cf. Lin and Bell[9]). The higher ratio obtained with Redux probably reflects its higher flexibility since this will allow a greater degree of peel to be tolerated than in the case of the brittle epoxy resin.

Thus, it is possible to reduce the isothermal and isochronous sets of data to a common scale by expressing the observed bond strengths as a percentage of the bond strength for a "fully" cured joint. Figure 5 illustrates this by plotting relative bond strength against T^* for both isochronous and isothermal cures. From this it is immediately evident that T^* does not fully characterize the undercured resin. A similar result is obtained by plotting relative bond strength

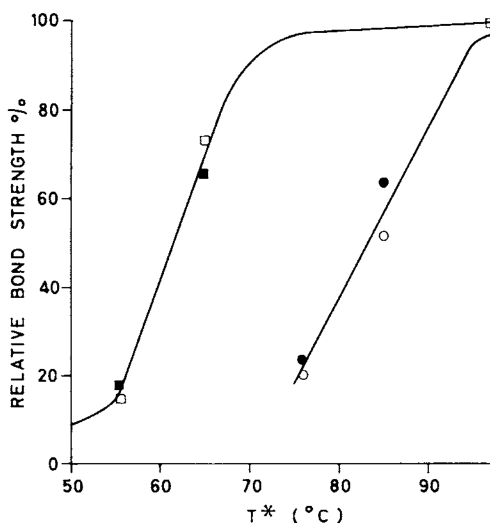


Fig. 5. Variation of bond strength with T^*, isochronous and isothermal data. Isochronous data: (○) single lap; (●) double lap. Isothermal data: (□) single lap; (■) double lap.

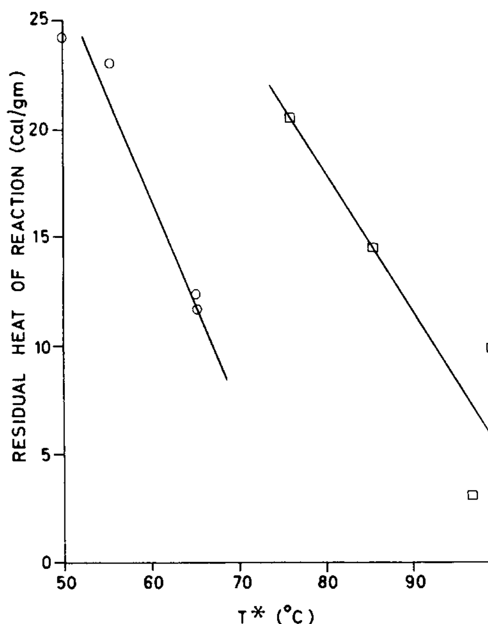
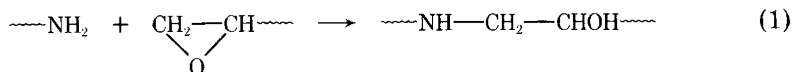


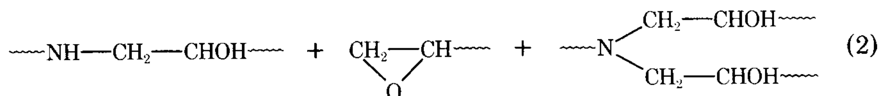
Fig. 6. Residual heat of reaction vs. T^*: (○) isochronous data; (□) isothermal data.

against residual heat of reaction. Thus, it is possible to produce joints in which the "state of cure," i.e., T^* or residual heat of reaction as measured by the DSC, is the same but which have greatly differing bond strengths.

The situation is somewhat improved when both T^* and the residual heat of reaction are considered together. A graph of residual heat of reaction versus T^* for the two cases (isothermal and isochronous) is presented in Figure 6. This shows that the two types of cure are distinct and can, in favorable circumstances, be differentiated from a knowledge of both T^* and the residual heat of reaction. The differences might, however be less where less extreme heating and cooling rates are used, as in normal practice in the laboratory and in industry. In these cases, joints are normally assembled in cold jigs which are then placed in an oven, and cooling is carried out at a natural rate in the jig.

The viscosity of the mix may limit the extent of crosslinking at low temperature. An investigation by Schechter et al.[10] suggests that reaction (1) is about ten times more rapid than reaction (2):





This implies a higher activation energy for reaction (2), and hence reaction (1) will predominate, particularly at low temperatures, giving an essentially linear polymer with fewer crosslinks than in the material cured at higher temperatures. The formation of a linear system may sterically hinder completion of the cross-

linking reaction. Thus, the two types of cure can give rise to different crosslinked structures having the same residual amount of reaction but different T^* values and different bond strengths (the relationship between T^* and bond strength will also differ for the two types of cure since different structures are being compared).

The residual heat of reaction is a "chemical" measure of the amount of further reaction which can occur, reactions (1) and (2); while T^* is a "physical" measure of the degree of crosslinking. Both residual heat of reaction and T^* correlate well with adhesive bond strength for bonds prepared under similar conditions. This is to be expected if the mode of bond failure is largely cohesive, i.e., if bond performance is determined by the properties of the resin rather than the properties of the interface.

CONCLUSIONS

Differential scanning calorimetry can be used to assess both the residual heat of reaction and the T^* of an epoxy resin. Both of these parameters may be used to monitor the cure of the resin, but the state of cure can only be specified by observation of both parameters. This technique is of no value in the case of Redux (a phenol-formaldehyde/poly(vinyl formal) adhesive) because of volatile emission during cure.

In the case of single-lap joints using the epoxy resin, bond failure is cohesive in the range 70–90% cure and becomes adhesive in the range of 90–100% cure. For double-lap joints, failure is essentially cohesive for all states of cure. The constant single/double bond strength ratio is also consistent with these observations, the different value of this constant for the Redux system being explained by the latter's greater flexibility and tolerance to peel forces.

The experiments on delayed cure emphasize the importance of minimizing such delays in both laboratory and industrial practice.

References

1. R. A. Fava, *Polymer,* **9,** 137 (1968).
2. Ministry of Defence (Army Department) QAD(Mats) Report No. 170, Royal Arsenal East, Woolwich, London SE18 6TD, England (1970).
3. Ministry of Defence (Army Department) QAD(Mats) Report No. 187, Royal Arsenal East, Woolwich, London SE18 6TD England (1972).
4. J. M. Barton, *J. Macromol. Sci. Chem.,* **A8** (1), 25 (1974).
5. C. L. Brett, *J. Appl. Polym. Sci.,* **18,** 315 (1974).
6. C. W. Jennings, *J. Adhesion,* **4,** 25 (1972).
7. P. E. Cassidy, J. M. Johnson, and C. E. Locke, *J. Adhesion,* **4,** 183 (1972).
8. E. Orowan, *J. Franklin Soc.,* **290,** 493 (1970).
9. C. J. Lin and J. P. Bell, *J. Appl. Polym. Sci.,* **16,** 1721 (1972).
10. L. Schechter, J. Wynstra, and R. P. Kurkjy, *Ind. Eng. Chem.,* **48,** 94 (1956).

Received April 17, 1975
Revised June 18, 1975