Bonding of carbon fibre composites with an epoxide–isoprene copolymer

Derek M. Brewis, John Comyn and John R. Fowler
School of Chemistry, Leicester Polytechnic, Leicester LE1 9BH, UK
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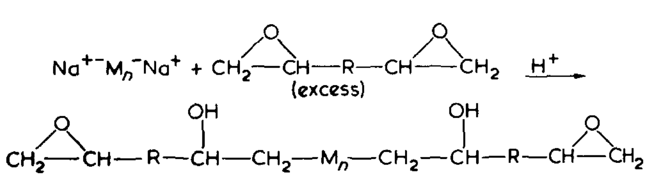
The use of an isoprene modified epoxide resin for bonding carbon fibre reinforced plastics (*CFRP*) is described. A detailed study is given of variables affecting the joint strengths with adhesives based on this epoxide. It is shown that a critical optimum cure exists for the composite matrix resin that was used. The importance of correct surface pretreatment is demonstrated. The modified epoxide resin forms the basis of useful room temperature adhesives for *CFRP*. However, the heat distortion temperatures are relatively low.

INTRODUCTION

Carbon fibre reinforced plastics (*CFRP*) have a considerably higher specific stiffness than common engineering metals and glass fibre composites. Despite their high cost, carbon fibre composites are being used increasingly in aeronautical and sports applications. There are also many potential applications in chemical, marine and mechanical engineering. The very high specific stiffness is usually the key property but the low coefficient of friction of the composites will be useful in certain applications.

Epoxide resins are by far the most widely used matrices in carbon fibre composites due to a unique combination of properties. Many curing systems exist giving a range of mechanical and thermal properties. No volatile by-products are formed on curing and the shrinkage is relatively low. The adhesion to the fibres is good and cured epoxides are relatively stable to adverse environmental conditions.

There will be an increasing need to bond *CFRP* to certain metals and to itself. Epoxide adhesives generally give high shear strengths but due to their lack of flexibility, the peel and impact strengths are often low. In an attempt to increase flexibility, Richards and coworkers copolymerized epoxide resins with butadiene or isoprene[1–3]. A dianion, based on isoprene or butadiene, was reacted with an excess of diepoxide which was predominantly the diglycidyl ether formed in the reaction between bisphenol A and epichlorohydrin. Polymers with a rubbery central block resulted:



Adhesives based on these modified epoxides showed promise for the bonding of metals[1,3].

Preliminary work showed that an adhesive based on a copolymer containing isoprene gave encouraging results when used for bonding *CFRP*[4]. The formulation developed at the Royal Aircraft Establishment, Farnborough, consists of: 100 g, diglycidyl ether–isoprene copolymer; 30 g, Ajicure B001; 40 g, Aluminium powder 240/dust.

The present paper describes a detailed study of several factors which affect adhesion levels achieved between adhesives based on this copolymer and *CFRP*. The variables investigated include the nature of the curing system, the curing conditions both for the adhesives and the resin in the *CFRP* composite and the fillers used in the adhesive. Heat distortion temperatures of the adhesives were measured using thermomechanical analysis.

EXPERIMENTAL

Materials

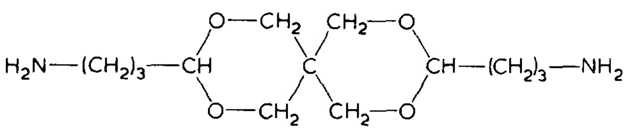
Carbon fibre tapes 25 mm wide and square woven from type II carbon fibres were supplied by James Carr and Sons Ltd, and were lightly sized with an epoxide resin.

The laminating resin was Epikote 828 cured with Epikure 114 hardener. For comparison Epikote 162 resin with Epikure 113 hardener was used in one case. Epikote and Epikure are trade names of Shell Chemicals UK Ltd.

The epoxide resin for the adhesive was the product of copolymerizing the diglycidyl ether of bisphenol A with isoprene[1–3]. The resin consists of 2 phases which separate into 2 layers on standing, the upper isoprene rich layer occupying about 10% of the total volume. The modified epoxide resin was provided by Dr D. H. Richards.

Ajicure B001 and di-(1-aminopropyl-3-ethoxy) ether were used as hardeners for the epoxide resin.

Ajicure B001 was obtained from Albright and Wilson Ltd. Its amine equivalent weight is 135 and the following molecule is thought to be a major component[5]:



The following fillers were used: aluminium powder (240 to dust), stainless steel powder (diameter ⩽100 μm), Ballotini spheres (lead glass, 0.105 mm diameter), asbestos powder, (grease free, density = 560 kg/m^3, particle size 200 mesh). The Ballotini spheres were degreased in a Soxhlet apparatus for 6 h with methylene chloride.

Production of test-pieces

Test-pieces were produced by the leaky mould method described by Phillips[6], using 25 mm carbon fibre square weave tape. The laminating resin was Epikote 828 cured with Epikure 114 in the ratio 100:38 by wt; this was brushed vigorously into the lengths of tape from both sides until the fibres were completely wetted. Four such impregnated lengths were laid into each cavity of an aluminium mould, which had previously been coated with aluminium stearate grease. Sufficient weights were placed on the mould to obtain a pressure of ~0.03 MN/m^2 and left overnight at room temperature. Subsequent post-curing was carried out in an oven. The following symbols are used to describe conditions of post-curing: θ_c, temperature of post-cure of the carbon fibre composite test-piece; t_c, duration of post-cure of carbon fibre composite test-piece.

After post-curing the mould was allowed to cool for 1 h before removal of the test-pieces. These were 3.0 mm thick and were cut into lengths of 137 mm.

Composite surfaces were prepared for bonding in the following way: they were first cleaned with a tissue soaked in 1,2-dichloroethane and then rubbed with silicon carbide paper (240 grade). The surface was wiped with a tissue soaked in butanone until no further particles were removed. Test-pieces were used within 3 h of cleaning.

For the purpose of comparison some composite surfaces were prepared by an alternative procedure, i.e. *CFRP* was abraded with wet 600 grade silicon carbide paper until a continuous water film was obtained. Loose material was then removed with a tissue soaked in acetone.

Adhesive formulation, application, curing and testing

With Ajicure hardener the following formulation was used: 100 g, diglycidyl ether–isoprene copolymer; 30 g, Ajicure B001; 40 g, aluminium powder 240/dust. The copolymer was heated to 50°C and the aluminium powder was added and thoroughly mixed. This mixture was allowed to cool to room temperature. The hardener was then added and the mixture stirred thoroughly.

Di-(1-aminopropyl-3-ethoxy) ether, DAPEE, was used as an alternative hardener to Ajicure B001. The same mixing procedure was employed but the amount of hardener used was 25.2 g instead of 30 g.

Where adhesives were compounded using fillers other than aluminium powder, the volume percentage of filler was kept the same.

The adhesive was spread thinly on to the test-pieces with a glass rod, the joint area being 625 mm^2. Two lengths of 0.125 mm wire were placed on one of the test-pieces and the joint completed. The purpose of these wires was to control the glue line thickness; they were positioned across the joint and extended from one side of the joint to the other. Excess adhesive was wiped from the sides of the joint with a tissue, and the whole assembly transferred to a curing jig, which ensured correct alignment of the adherends. A 2 kg weight was placed on each joint to provide a bonding pressure of about 0.03 MN/m^2.

The curing jig was placed in an oven at a temperature of 20°C for 16 h. Post-curing then took place under chosen conditions. Upon removal from the oven the jig was left for 1 h to cool. The bonded test-pieces were then removed. The following symbols are used to describe curing conditions of adhesive joints; θ_j, temperature of post-cure of adhesive joint, or a sample of the adhesive; t_j, duration of post-cure of adhesive joint, or a sample of the adhesive.

Joints were tested to destruction using a Hounsfield W Tensometer at a strain rate of 0.104 mm/sec.

Measurement of heat distortion temperatures

Samples of adhesive were placed in small aluminium cans of 8 mm diameter and 2 mm deep and were cured in the same manner as the adhesive joints. Heat distortion temperatures were then determined with a Du Pont Thermomechanical Analyser, using the instrument as a penetrometer, at a scan rate of 10 K/min, and scan ranges were generally from 0° to about 80°C. In a few cases however, scanning was from liquid nitrogen temperature. A 10 g weight was loaded onto the probe. It is estimated that T_d can be measured in this way to within ±2K. This is shown by error bars in *Figures 8–10*.

RESULTS AND DISCUSSION

Various types of joint failure were observed and these are given the following symbols: *I*, apparent interfacial failure; *C*, cohesive failure of the adhesive; *M*, material failure of laminate.

The vertical lines given in *Figures 1–7* show the mean, maximum and minimum values obtained.

Curing of matrix resin

Before investigating the effects of adhesive composition and curing conditions of the adhesive, the curing of the composite was examined; these results are given in *Figure 1*.

These results show there are optimum curing conditions for the Epikote 828–Epikure 114 systems as far as the resultant joint strength is concerned. At a post-curing temperature of 80°C, increasing the time of post-cure can result in much lower joint strengths. It is very unlikely to be due to the decomposition of the epoxide resin. It could be because of decreased reactivity of the composite towards the adhesive due to more complete curing at higher times leaving fewer reactive groups; this is supported by the change in joint failure from partly cohesive to interfacial.

With the Epikote 162–Epikure 113 system only one post-cure was used (3 h at 100°C), but the mean joint strength (18.6 MN/m^2) was greater than any achieved with Epikote 828–Epikure 114. Thus joint strength is considerably affected by the nature of the composite and its degree of cure.

Surface preparation

When the alternative surface preparation was used after post-curing the joints for 6 h at 80°C an average shear strength of 10.3 MN/m^2 was obtained, i.e. 32% less than with the usual pretreatment. There are at least two reasons

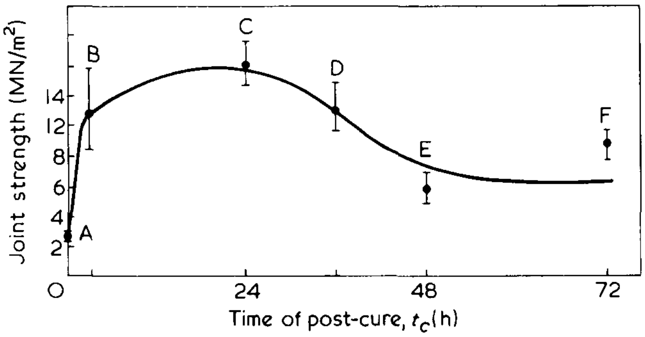


Figure 1 Dependence of joint strength on time of post-cure of composites at 80°C. Adhesive: modified epoxide with Ajicure hardener (θ_j = 60°, t_j = 3 h). Joint failure: A, *M*; B, *I* + *C*; C, *I* + *M*; D, *I*; E, *I* ; F, *I*

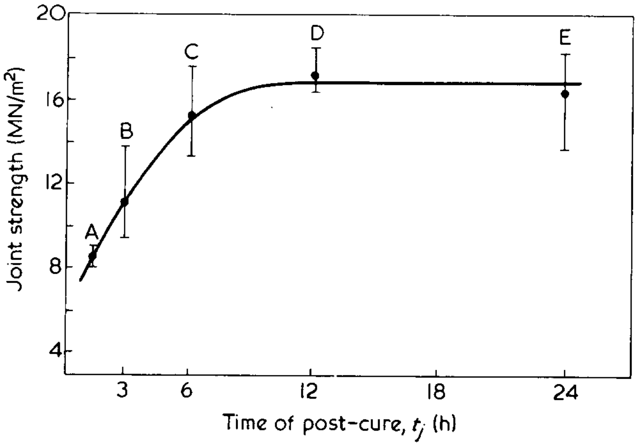


Figure 2 Dependence of joint strength on time of post-cure at 60°C. Adhesive: modified epoxide with Ajicure hardener (θ_c = 80°C, t_c = 3 h). Joint failure: A, *I*; B, *I* + *C*; C, *I* + *C* + *M*; D, *I* + *M*; E, *I* + *M*

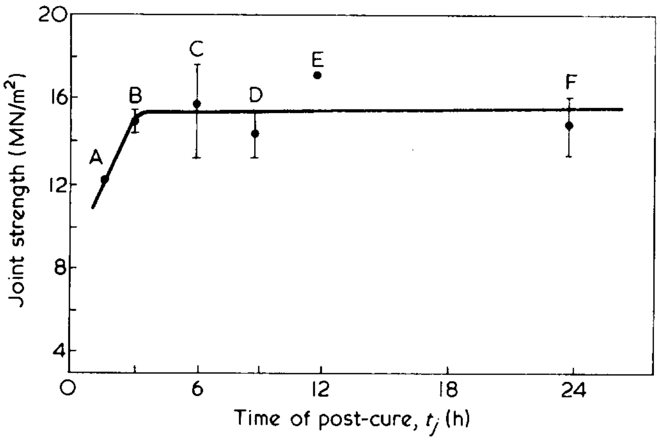


Figure 3 Dependence of joint strength on time of post-cure at 80°C. Adhesive: modified epoxide with Ajicure hardener (θ_c = 80°C, t_c = 3 h). Joint failure: A, *I*; B, *I* + *C*; C, *I* + *M* + *C*; D, *I* + *M* + *C*; E, *I* + *M* + *C*; F, *I* + *M* + *C*

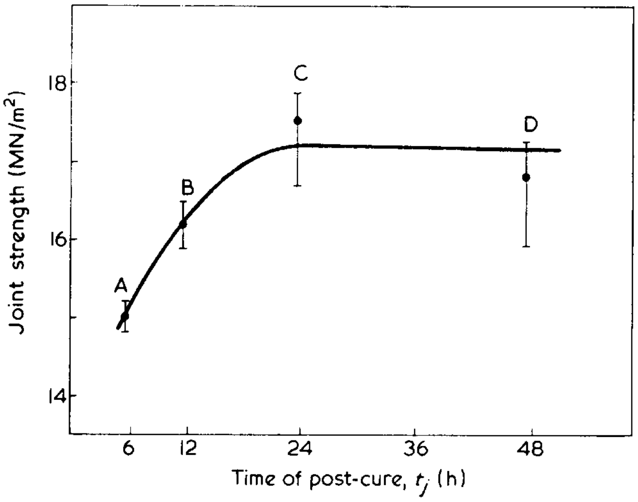


Figure 4 Dependence of joint strength upon time of post-cure at 60°C. Adhesive: modified epoxide with DAPEE hardener (θ_c = 80°C, t_c = 3 h). Joint failure: points A–D, *M* + *C*

for the lower values. The stearate grease may not have been completely removed; in the usual pretreatment, the test-pieces are first cleaned with 1,2-dichloroethane. Alternatively, the difference in joint strength may be due to a difference in surface roughness as different grades of carbide paper were used in the two methods. The failure mode with the alternative surface preparation was completely interfacial, whilst failure was predominantly material and cohesive with the usual pretreatment.

Curing of the adhesive

The effect of curing conditions on joint strengths is given in *Figures 2* and *3* for Ajicure when θ_j = 60° and 80°C respectively. The corresponding results for DAPEE are given in *Figures 4* and *5*. The dependence of joint strength upon temperature of post-cure when using Ajicure is shown in *Figure 6*.

With Ajicure, increased times of post-cure at a given temperature result in increased joint strengths up to a maximum; at 60° and 80°C maxima are reached after about 12 and 3 h respectively (*Figures 2* and *3*). The maximum at 60°C is higher (16.8 MN/m^2) than that at 80°C (14.8 MN/m^2). When the adhesive is post-cured at 120° and 140°C for 3 h significantly lower joint strengths are obtained (*Figure 6*). This is unlikely to be due to decomposition of the adhesive but may be due to vaporization of

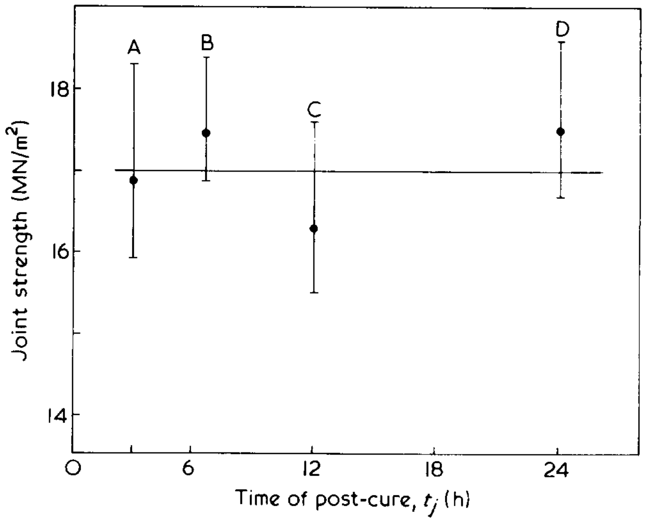


Figure 5 Dependence of joint strength upon time of post-cure at 80°C. Adhesive: modified epoxide and DAPEE hardener (θ_c = 80°C, t_c = 3 h). Joint failure: points A–D, *M* + *C*

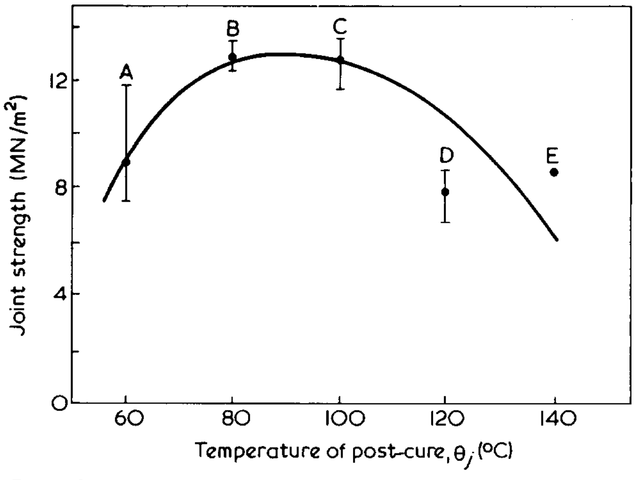


Figure 6 Dependence of joint strength upon temperature of post-cure. Adhesive: modified epoxide with Ajicure hardener (θ_c = 80°C, t_c = 3 h, t_j = 3 h). A, *I* + *C*; B, *I* + *C*; C, *I* + *C* + *M*; D, *C*; E, *I* + *C*

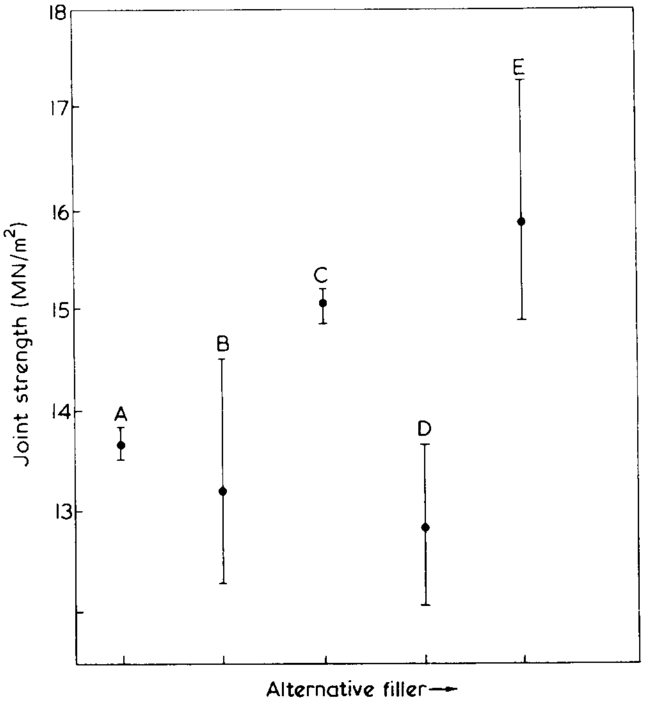


Figure 7 Effect of fillers on bond strength of joint bonded with modified epoxide and DAPEE (θ_c = 80°C, t_c = 3 h, θ_j = 80°C, t_j = 3 h). A, *M* + *C*, bentonite; B, *M* + *C*, stainless steel; C, *M* + *C*, asbestos; D, *C*, Ballotini; E, *M* + *C*, aluminium

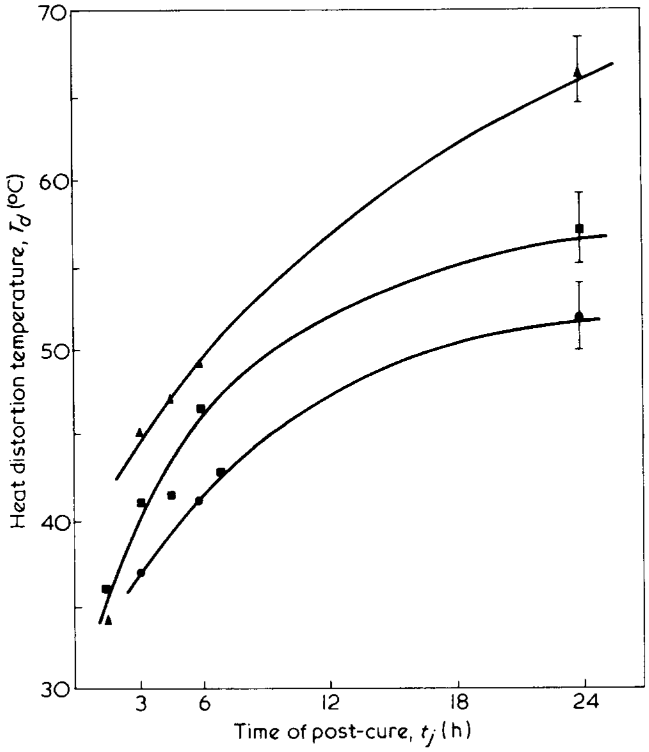


Figure 8 Dependence of heat distortion temperature upon cure time for modified epoxide resin and Ajicure hardener. Probe weight = 10 g. Values of θ_j: ●, 60°; ■, 80°; ▲, 100°C

a component in the Ajicure with the subsequent formation of voids.

With DAPEE (*Figures 4* and *5*), maximum joint strength is obtained after about 24 h post-cure at 60°C and within 3 h at 80°C. There is no significant difference in the values of maximum joint strengths at the two temperatures (~17 MN/m^2).

Alternative Fillers

The effect of alternative fillers is given in *Figure 7*.

The limited results of joint strengths with other fillers in *Figure 7* indicate that aluminium and asbestos powders give the highest joint strengths at this filler volume percentage. However, further work with the other fillers, e.g. using coupling agents with the Ballotini beads, could give a different picture.

It is interesting to note that with bentonite and asbestos the variabilities in the results are much less than with the other fillers. However, it is not possible to draw firm conclusions from the limited data.

Heat distortion temperatures

Heat distortion temperatures for the adhesives are given in *Figure 8* (Ajicure) and *Figures 9* and *10* (DAPEE).

Figures 8–10 show the tendency of heat distortion temperatures to rise initially with the time of post-cure t_j; this is in accord with T_d increasing with the degree of crosslinking. When DAPEE is the hardener, T_d reaches a plateau, after which further post-curing leads to no further increase in T_d The plateau is reached after ~18 h at 60°C; this may be compared with the time to reach the plateau on the plot (*Figure 4*) of joint strength against t_j for the same adhesive at 60°C. After taking the uncertainties of estimating these times into account, it seems that they are in agreement.

When post-curing at 80°C with DAPEE hardener, the plateau on the plot of strength against t_j (*Figure 5*) is reached within a few hours. This time is broadly in agreement with the time to reach maximum T_d (*Figure 10*).

There is some cohesive failure in all the joints reported in *Figure 4*; the failure stress of these adhesives seems to be linked with the degree of crosslinking.

With Ajicure hardener (*Figure 8*) plateaus are not reached during 24 h of postcuring, whilst plots of joint strength (*Figures 2* and *3*) show plateaus after approximately 12 h (at 60°C) and 3 h (at 80°C). Modes of failure are more mixed than with DAPEE. Only half of the joints show

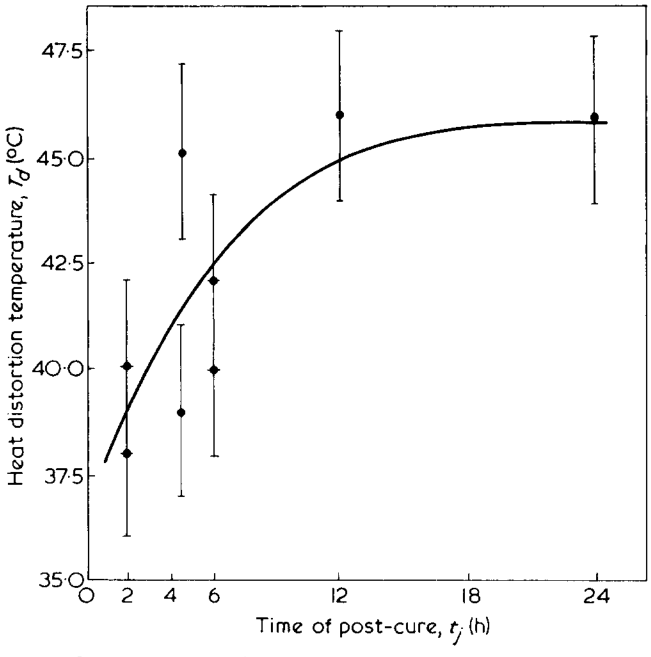


Figure 9 Dependence of heat distortion temperature upon cure time for modified epoxide resin and DAPEE hardener post-cured at 60°C. Probe weight = 10 g

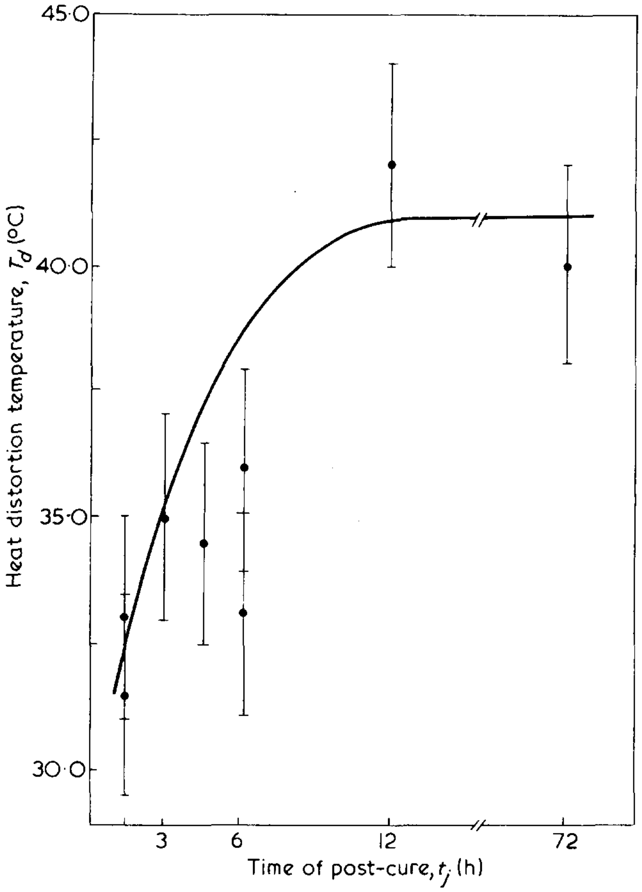


Figure 10 Dependence of heat distortion temperature upon cure time for modified epoxide and DAPEE hardener post-cured at 80°C. Probe weight = 10 g

some cohesive failure, whilst all of them show some interfacial failure.

With DAPEE hardener, values at the plateaus are 41° and 46°C, and these are obtained within moderate post-curing times. Higher T_d values can be obtained using Ajicure hardener only after extended post-cures. Ajicure contains less flexible molecules than DAPEE and so would be expected to produce higher T_d values. Attainable heat distortion temperatures during moderate post-curing times are less than 50°C, a factor which would limit the use of the modified epoxides in structural adhesives. It is possible that higher T_d values might be obtained with the less flexible molecules of aromatic hardeners.

Attempts to measure glass transition temperatures using differential scanning calorimetry were unsuccessful.

CONCLUSIONS

(1) The curing conditions of the matrix resin have an important effect on the resultant lap shear strength; an optimum cure exists for the Epikote 828–Epikure 114.

(2) Correct surface pretreatment of the *CFRP* is critical and in particular effective removal of mould release agent is essential.

(3) The adhesives based on the modified epoxide are satisfactory for bonding *CFRP* to *CFRP* at room temperature. However, the relatively low heat distortion temperatures would limit their use as structural adhesives. However, aromatic hardeners might increase T_d by a sufficient degree to overcome this defect.

(4) Initial tests showed that a range of fillers can be used in the adhesives.

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REFERENCES

1 Cunliffe A. V., Huglin, M. B., Pearce, P. J. and Richards, D. H. *Polymer* 1975, **16**, 654
2 Cunliffe, A. V., Huglin, M. B., Pearce, P. J. and Richards, D. H. *Polymer* 1975, **16**, 659
3 Cunliffe, A. V., Huglin, M. B., Pearce, P. J. and Richards, D. H. *Polymer* 1975, **16**, 665
4 Phillips, L. N. personal communication
5 Berry, D. B. S., Buck, B. I., Cornwell, A. and Phillips L. N. 'Handbook of Resin Properties Part A: Cast Resins', Yarsley Testing Laboratories, Ashtead, UK, 1975, p 35
6 Phillips, L. N. *Trans. J. Plast. Inst.* 1967, **35**, 589