An aliphatic amine cured rubber modified epoxide adhesive: 2 Further evaluation

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A resin which consists of the product of reacting the diglycidyl ether of bisphenol A with a dicarboxy-terminated butadiene–acrylonitrile copolymer has been evaluated as an adhesive when hardened with di(1-aminopropyl-3-ethoxy) ether and filled with ballotini glass spheres. The resistance of the adhesive to both shear and peel has been examined. Thermomechanical analysis shows the adhesive to have two transition temperatures; this is interpreted in terms of the adhesive consisting of two phases

INTRODUCTION

In part 1[1] the synthesis of a diepoxide-terminated butadiene–acrylonitrile resin was described, along with some evaluation of the use of this product as an adhesive with di(1-aminopropyl-3-ethoxy) ether (DAPEE) as hardener. The adhesive was evaluated with aluminium alloy adherends in single lap and peel joints. Surfaces were prepared by degreasing with chloroform followed by sandblasting, and curing was for 72 h at room temperature. The effects of variables during the synthesis of the diepoxide upon the strengths of peel and lap joints were examined, the variables being the amounts of dicarboxy-terminated butadiene–acrylonitrile (CTBN) and 2,4,6-tris(dimethylaminomethyl) phenol catalyst in the reaction mixture and the time of precure.

Now we report further examination of the adhesive properties of a resin prepared by the uncatalysed reaction of CTBN with the diglycidyl ether of bisphenol A (DGEBA) in the ratio of 15 to 100 parts by weight. Here the adhesive has been cured at 80°C rather than room temperature. Examination has been made of the strengths of single lap and peel joints, heat distortion temperatures of the adhesives, and resistance to elevated temperatures and high humidity.

EXPERIMENTAL

Strips of BS3 L73 aluminium alloy (25 mm wide x 1.7 mm thick) were the adherends for single lap joints. In peel joints BS2 L61 aluminium alloy was used in thicknesses, 12 and 24 swg (2.64 and 0.56 mm). Carbon fibre reinforced plastic (CFRP) was supplied by Mr L. N. Phillips of the Royal Aircraft Establishment and consisted of unidirectional HT-S fibre embedded in Shell Epikote 210† epoxide resin cured with 3 g of boron trifluoride monoethylamine per 100 g of resin. Its nominal fibre content was 60% by volume and it was 2 mm thick.

Lead glass ballotini spheres were of diameter 105–210 μm and coated with 3-aminopropyl triethoxy silane adhesion promoter. The ballotini was separated into 3 fractions (< 105 μm, 105–125 μm > 125 μm) by sieving. This involved the use of two sieves of nominal aperture size 125 and 105 μm. The ballotini spheres were shaken mechanically in the sieves for 30 min in 100 g batches. The middle fraction (105–125 μm) was used as an adhesive filler.

The resin was prepared by the authors of part I by reacting CTBN with DGEBA in the weight ratio of 15 to 100 in the absence of a catalyst. The reaction mixture was heated to 150°C and maintained at this temperature for 2½ h before being allowed to cool.

Surface preparations

Light alloy adherends for lap joints were surface treated in the following way. After degreasing in a Soxhlet apparatus with trichloroethylene, they were immersed in a distilled water solution containing sulphuric acid (15% by vol) and chromium trioxide (50 g/dm^3) for 20 min at 60°–65°C. Thorough rinsing in cold tap water was followed by drying in an oven. Adherends for peel joints were surface treated in a similar manner, but here degreasing was by wiping with a tissue soaked in butanone. CFRP adherends were first wiped with a tissue soaked in 1,2-dichloroethane and then rubbed with silicon carbide paper (240 grade). Finally the surface was wiped with a tissue soaked in butanone until no further particles were removed. Treated surfaces were used as soon as possible after preparation.

Adhesive preparation

The adhesive consisted of the rubber-modified epoxide resin, DAPEE hardener and ballotini filler. These were mixed at room temperature and then spread thinly on both adherends with a glass rod.

Single lap joints

Ten single lap joints could be stacked vertically in a curing jig which ensured the correct overlapping of joints (12.5 x 25 mm) during curing, which was at 80°C. Polyethylene films divided each joint from its neighbour, and a silicone rubber block placed on top of the stack could be pressed against the joints by two springs which pressed against a bar laid across the block. A pressure of 0.12 MN/m^2 was applied in this way. After curing in an oven, joints were allowed to cool for 60 min before shearing to destruction in a

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† Trade name of Shell Chemicals UK Ltd.

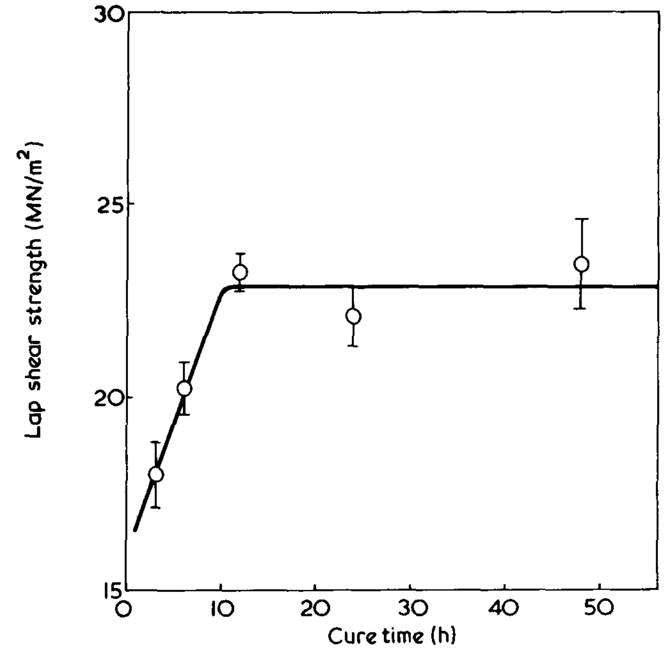

Figure 1 Dependence of lap shear strength on cure time at 80° C (24.2 g DAPEE and 36.7 g ballotini per 100 g resin). Error bars indicate standard deviations

Hounsfield Tensometer (type W), with a crosshead speed of 0.1 mm/sec. Loads at failure were recorded.

Peel joints

Two rectangular sheets (254 mm x 203 mm) of aluminium alloy, one of 12 swg (2.64 mm) and one of 24 swg (0.56 mm) were spread with adhesive so that a strip 50 mm wide across one end was free of adhesive; this later provided a tag which could be bent at 90° for insertion into the jaws of the testing instrument. The sheets were sandwiched together so as to minimize the trapping of air bubbles in the adhesive, and the sandwich was cured in a hydraulic press under 0.24 MN/m^2 pressure at 80°C. After curing and cooling, the sandwich was cut into strips 254 mm x 25 mm, discarding the 12 mm strip along each side. Cutting was by a bandsaw, and it is clearly important not to introduce stress into the adhesive during sawing. The following conditions of cutting were recommended[2] as suitable: band speed of 2.5 m/sec, with 8 teeth per cm of band.

The 24 swg (0.56 mm) member was bent at 90°C and peeled from the 12 swg (2.64 mm) member using an Instron 1026 tensile testing instrument with the peel test fixture described in DTD 5577[3]. The peeling rate was 2.8 mm/sec and during peeling it was ensured that the specimen was held at 90° to the axis of loading. An autographic recording of the loading was taken.

Exposure of lap joints to humidity and elevated temperature

Some lap joints were sheared to destruction after storage in an air oven at 50° or 100°C for 1000 h. Other joints were exposed to wet air (96% r.h.) at 45°C for 1000 h. Humidity was maintained either in a Gallenkamp humidity oven or in a desiccator containing a saturated solution of sodium sulphate contained in an oven[4] at 45°C.

Measurement of glue-line thickness

Some lap joints were cut so as to produce two faces, which after polishing on a Metaserv rotary pregrinder could be viewed under a Hilger and Watts surface-finish microscope. Glue-line thicknesses were measured at equally spaced points along the line using the micrometer stage of the microscope. A similar procedure was used to examine the cut edge of some peel joints.

Thermomechanical analysis (t.m.a.)

Samples of adhesive were cured in small aluminium cans (8 mm diameter, 2 mm deep). These samples were examined in a du Pont thermomechanical analyser used as a penetrometer with a 10 g weight loaded on the probe. The scan range was from liquid nitrogen temperature to about 80°C, and the scan rate was 10°C/min.

RESULTS AND DISCUSSION

Cure time

The formulation first used was resin 100 g, DAPEE 24.2 g, ballotini 36.7 g, and shear strengths of lap joints were measured after curing for various times at 80°C. Between four and seven joints were cured at each time and their failure was 90–95% cohesive, the remaining 5–10% being interfacial. Results are shown in *Figure 1* which shows that a maximum joint strength of 22.9 MN/m^2 is obtained after about 12 h. In subsequent work curing was for 24 h at 80°C.

Adhesive formulation for lap joints

The amount of hardener was varied between 19.4 and 30.1 g per 100 g resin, while the amount of ballotini was held at 36.7 g per 100 g resin. The strengths of the resulting lap joints are shown in *Figure 2*, from which a minimum strength is evident at about 25 g DAPEE per 100 g resin. Between six and eleven joints were examined at each composition. Joint failure was 95% cohesive.

The amount of ballotini was varied between 1.0 and 37.0 g per 100 g resin, while the amount of DAPEE was 26.6 g per 100 g resin. *Figure 3* shows that shear strength decreases with increasing ballotini content, presumably due to increased stress concentration around ballotini spheres. In subsequent work the amount of ballotini was kept at 2 g per 100 g resin as this amount was judged as sufficient to control glue line thickness.

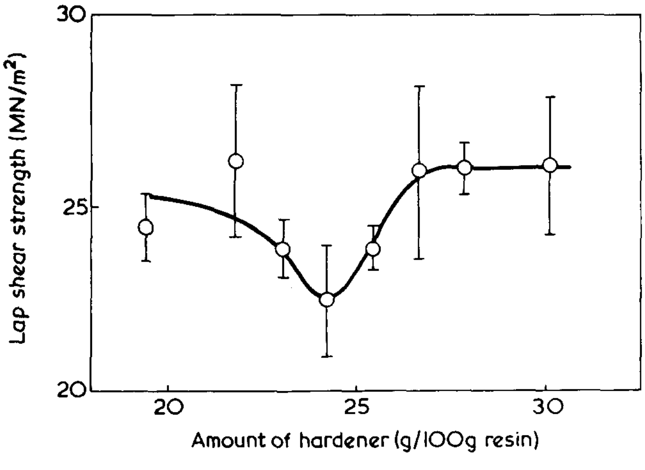

Figure 2 Dependence of lap shear strength on the amount of DAPEE hardener (36.7 g ballotini per 100 g resin, cured for 24 h at 80° C). Error bars indicate standard deviations

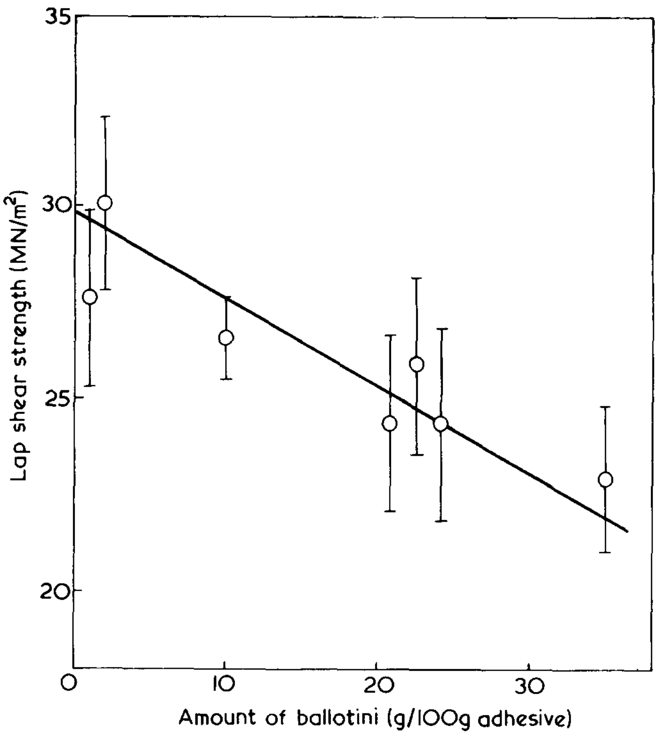

Figure 3 Dependence of lap shear strength on the amount of ballotini filler (26.6 g DAPEE per 100 g resin, cured for 24 h at 80° C). Error bars indicate standard deviations

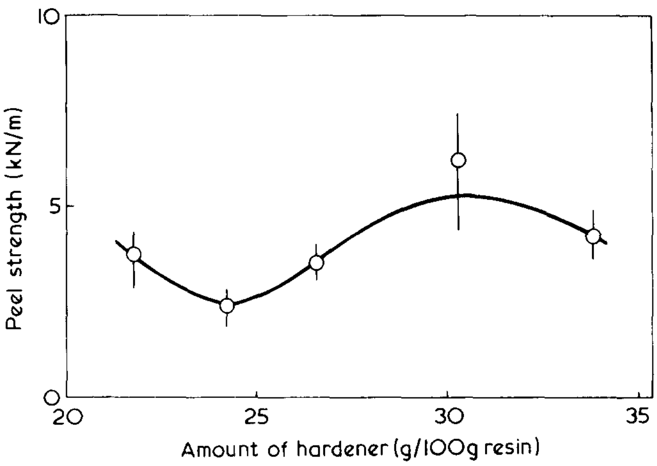

Figure 4 Dependence of peel strength on the amount of DAPEE hardener (2.4 g ballotini per 100 g resin, cured for 24 h at 80° C). Error bars indicate average maximum and minimum peel strengths

Adhesive formulation for peel joints

Each sandwich provided seven peel specimens, and one sandwich was used for each formulation. The effect of the amount of hardener was examined by using the same amounts of hardener as were used with lap joints. Some scatter was evident in the autographic recordings, and for each recording maximum, minimum and mean peel strengths were estimated. However, the first 25 mm of each peel were disregarded, as were minima which were clearly due to the presence of large bubbles in the adhesive. Joints failed interfacially. Results are shown in *Figure 4* in which the points are the average of the seven mean peel strengths, and the error bars indicate the averages of the seven maxima and minima respectively. Comparison of *Figure 4* and *Figure 2* shows the same minimum of joint strength at about 25 g DAPEE per 100 g resin.

Glue-line thicknesses

Glue-line thicknesses of two lap joints which contained 2 g ballotini per 100 g resin were examined at 19 positions in each joint. The mean thicknesses of the joints were 0.112 ± 0.004 μm and 0.110 ± 0.007 μm. One peel sandwich was examined at 79 places in all, and glue-line thicknesses were in the range 0.112 to 0.206 μm, the thicker glue lines being towards the centre of the sandwich. Upon measuring the peel strengths of these joints (the middle result in *Figure 4*) there was no evidence that peel strength depended upon glue-line thickness. Clearly, with the smaller lap joints, the addition of a small amount of ballotini provides good control of glue-line thickness. Poorer control with the much larger sandwiches probably reflects difficulties associated with adherend flatness.

Thermomechanical analysis

The cured adhesive exhibits two transitions when examined by thermomechanical analysis, e.g. *Figure 5*, which indicates the presence of two phases. The upper transition which occurs at about 50°C is the heat distortion temperature of the adhesive (T_d) and can be associated with softening of the epoxide matrix, while the lower transition at about −50°C can be associated with the glass transition temperature of a disperse rubbery phase. The upper transition varies with the amount of hardener in the adhesive (*Figure 6*), while the lower transition T_L shows no dependence upon the amount

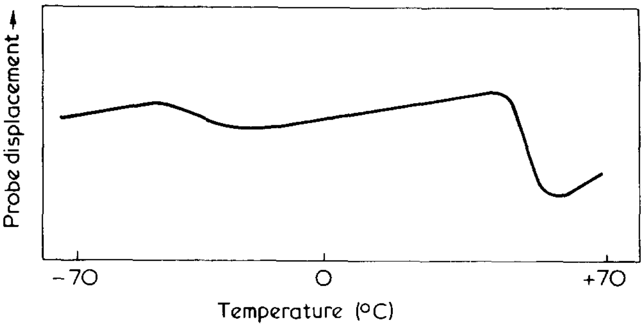

Figure 5 Thermomechanical analysis scan for adhesive (30.3 g DAPEE and 36.7 g ballotini per 100 g resin cured for 24 h at 80° C)

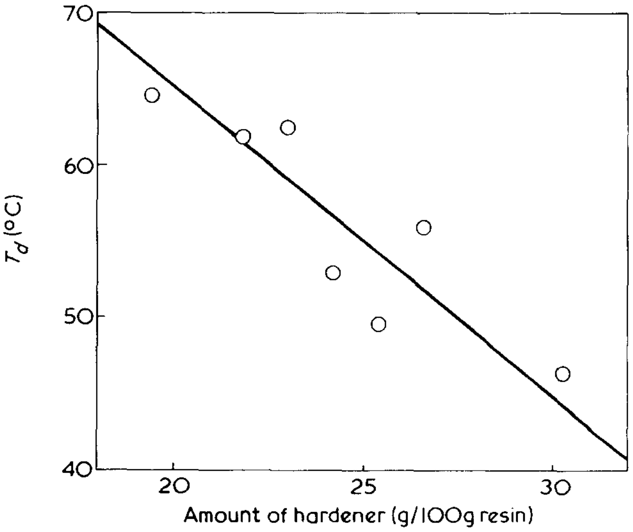

Figure 6 Dependence of heat distortion temperature upon the amount of hardener (36.7 g ballotini per 100 g resin, cured for 24 h at 80° C)

of hardener. T_L was −53° ± 6°C for the samples shown in *Figure 6*. T_d is depressed by increasing the amount of hardener; DAPEE is a long flexible molecule which is capable of plasticizing the cured epoxide matrix. As T_L is independent of the amount of hardener, it seems that the hardener is excluded from the rubbery phase, which is a copolymer of acrylonitrile and butadiene containing 18–19% of acrylonitrile. The glass transition temperatures of such copolymers depend upon composition according to the following equation[5]:

$$T_g(^\circ\mathrm{C}) = -85 + 1.40\ (\%\ \text{acrylonitrile})$$

which indicates that the value of T_g for the rubbery phase in the cured adhesive should be −59°C, in good agreement with the values of T_L observed.

Optimum formulation

The stresses which may be subjected to adhesive joints in service are generally mixed and variable, and so in selecting the best formulation, resistance of adhesive joints to both peeling and shearing forces should be considered. In this case the worst formulation is easiest to spot; it is that presented by the minimum in *Figures 2* and *4*. The shoulder on either side of this minimum provides improved resistance to shear and peel, but the shoulder at the lower amount of hardener has the advantage of having a higher heat distortion temperature. These factors, together with the consideration of the ballotini content, show that the optimum adhesive formulation is of resin 100 g, DAPEE 21.8 g, ballotini 2.4 g.

Effect of elevated temperature and high humidity

Exposure of lap joints prepared with the optimum formulation to elevated temperature lead to small increases in lap shear strength; joint strengths are given below.

Control	28.9 ± 2.8 MN/m^2	(26 joints)
1000 h at 50°C	30.9 ± 2.6 MN/m^2	(8 joints)
1000 h at 100°C	32.3 ± 3.8 MN/m^2	(8 joints)

T_d was not significantly changed by heat ageing.

Exposure to warm humid air leads to loss of joint strength, followed by slight recovery after drying for 24 h. Longer drying could well lead to greater recovery. Joint strengths were:

Control	29.4 ± 1.6 MN/m^2	(4 joints)
1000 h at 45°C, 96% r.h.	23.1 ± 1.6 MN/m^2	(4 joints)
1000 h at 45°C, 96% r.h. + 50°C in vacuum oven for 24 h	25.2 ± 2.6 MN/m^2	(4 joints)

CFRP adherends

The optimum adhesive gave a lap strength of 25.3 ± 2.6 MN/m^2 (6 joints) with CFRP adherends. Failure was totally interfacial.

CONCLUSIONS

The diepoxide-terminated butadiene–acrylonitrile can be used as an adhesive with DAPEE hardener and ballotini filler. It gives good lap shear strengths with light alloy (cohesive failure) and CFRP (interfacial) adherends.

Peel strengths with light alloy adherends were moderate and failure was interfacial, indicating the need for improved surface treatment.

The optimum formulation is resin 100 g, DAPEE 21.8 g, ballotini 2.4 g, and maximum joint strengths are obtained after curing for 24 h at 80°C.

The cured adhesive consists of epoxide matrix which has a heat distortion temperature of about 50°C, and a dispersed rubbery phase with a transition temperature at about −50°C.

The adhesive shows good resistance to high humidity and to elevated temperature.

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