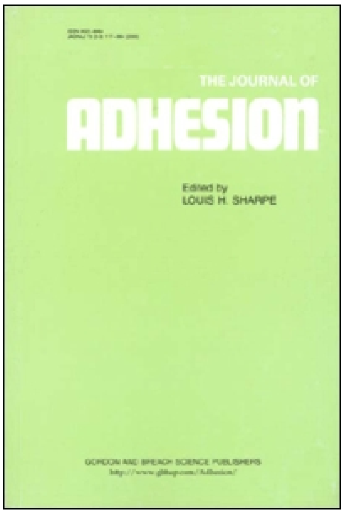

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Bubbles in Adhesive Joints with CFRP Adherends

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INTRODUCTION

During the course of a project in the Department of Aeronautics to explore the fatigue behaviour of adhesive bonded joints between carbon fibre and reinforced plastic adherends, double strap lap joints were prepared for initial proving of techniques. These were found to have strengths in shear which were both very variable and considerably lower than had been expected[1]. Failure generally occurred cohesively through the adhesive layer and examination of the failed surface revealed a considerable number of large bubbles within the cured adhesive. This phenomenon had only been reported on two previous occasions[2,3] although the effect of bubbles upon the stresses in a glue-line has been investigated.[4]

In order to achieve the potential strength of the bonds it was necessary to explore the origin of these bubbles and to devise techniques to eliminate or minimise their production and deleterious effects.

This paper describes the investigation of the chemical nature of volatile materials which lead to the formation of these bubbles.

MATERIALS

The carbon fibre reinforced plastic adherends were prepared from Fibredux 914C XAS prepreg manufactured by Ciba-Geigy Ltd. This is a modified epoxy resin with latent curing amine hardner, in which has been incorporated unidirectional fibres of high tensile, surface treated carbon fibre (Grafil XAS manufactured by Courtaulds Ltd) at 0.6 volume fraction fibre.

The test pieces were made by laminating 16 plies of prepreg. First a vacuum of 650–700 mm Hg was applied for an hour to consolidate the layers and remove entrapped air. Then heating was commenced at 2°C per minute until 140°C was reached when an air pressure of 60 lbf. in^{-2} was applied. Heating continued until a temperature of 175°C was attained. This temperature was held for 1 hour and then was allowed to fall to 60°C in 40 minutes. When the pressure was released the sheets were post-cured for 14 hours at 185°C in an oven. They were stored in a normal laboratory environment for up to 6 months before cutting to appropriate size and assembling into joints.

Alternative adherends used were glass microscope slides and aluminium alloy L72 (an aluminium-clad, aerospace alloy).

The adhesive used was Redux 308A manufactured by Ciba-Geigy Ltd. This is a modified epoxy resin with glass ballotini incorporated to control glue-line thickness, supplied in film form primarily designed for aerospace applications.

BONDING

The surface layer of resin was removed from the composite adherends by grinding. Other adherends were prepared for bonding by wiping the surfaces with an organic solvent to remove any grease.

Joints were made between various adherends under a pressure of 50 lbf. in^{-2} at a temperature of 150°C for 30 minutes.

EXPERIMENTAL

While the normal pattern of joint being used in the primary programme was double strap lap joints, for the investigation of the bubble problem ordinary single lap joints were used. When the composite adherends were dried at 40°C for ½ hour, joints were obtained which broke cohesively in the adhesive and contained a considerable number of large bubbles. These bubbles persisted in spite of drying the adhesive for ½ hour either in air or under vacuum. Indeed a number of variations were tried, solvent degreasing, grit blasting or grinding of the composite surface and the use of aluminium or glass as one of the adherends. The latter, of course, revealed the bubbles without the need to break the joint. The details of these, which are not relevant here, are all discussed in reference 1. Sufficient to say that it became quite clear that these bubbles in the joint were invariably occurring when at least one of the adherends was of carbon fibre reinforced plastic and were not associated with the adhesive.

There seemed to be three possible sources of volatile materials which might cause these bubbles:

(i) water which had been adsorbed (or absorbed) by the plastic,
(ii) air which had been entrapped in pores or surface irregularities in the surface of the plastic,
(iii) products released from within the plastic as a result of the procedure used in curing the adhesive.

Because of the high temperature used in the initial cure of the plastic matrix it is highly improbable that the reinforced plastic retains any moisture when it has first been made. However, the manufacturer's data indicates that the composites take up 0.7% of weight of water in 1000 hours at 20°C so that it appeared quite likely that moisture would have been absorbed during storage.

Drying at 150°C in air circulating oven showed a weight loss of 0.25% per hour initially, reducing to 0.03% per hour after 10 hours and reaching a total loss of 0.6% in 24 hours. In joints made with adherends which had been dried at 150°C for at least an hour the bubbles had been greatly reduced both in number and in size, but had not been eliminated.

Typical results are shown in Figures 1 and 2 where the bubbles with untreated and with dried composite are shown in joints after grinding away one adherend.

Complete elimination of bubbles was achieved by carrying out the curing with the joints under the direct pressure of 50 lbf. in^{-2} and additionally under an air pressure of 100 lbf. in^{-2}. This latter is conveniently greater than the saturated vapour pressure of water at 150°C (69 lbf. in^{-2}) and should effectively prevent the formation of bubbles of water vapour. Indeed no bubbles were observed when this technique was used.

To investigate the chemical nature of the volatile material which was liberated by the heating to cure the adhesive, a sample of the already cured composite was put into an RIIC GH-5 heated infra red cell and the temperature was raised to 150°C. The infra red absorption spectrum was determined with a Perkin Elmer 457 spectrometer. This gave

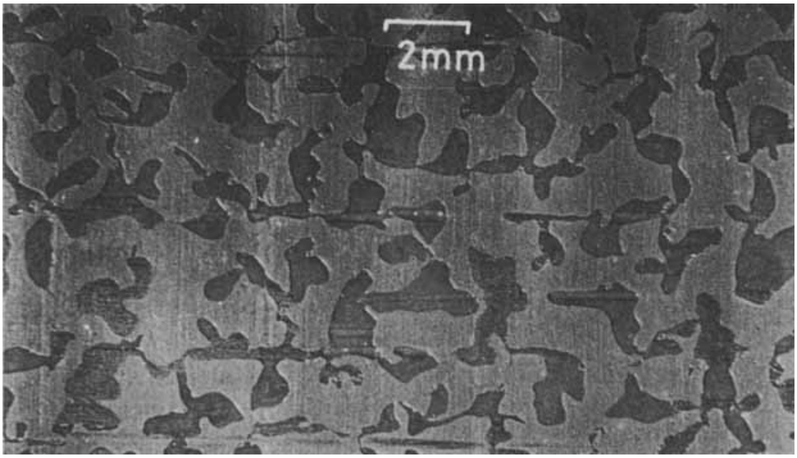

FIGURE 1 Large bubbles in carbon fibre composite joints made without drying the adherends.

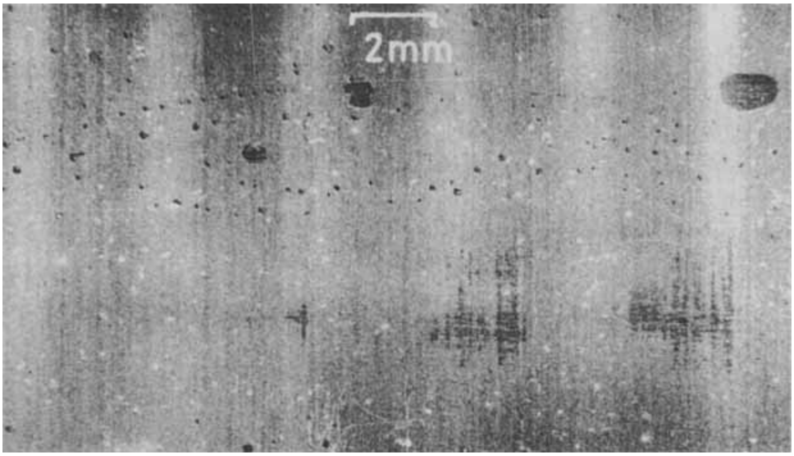

FIGURE 2 Small bubbles in carbon fibre composite joints made after drying the composite adherends at 150°C for 1 hr.

evidence of absorption bands but the signal to noise ratio was too small for clear assignments to be made, although there were indications of hydroxyl, carbonyl and methyl groups. Increasing the temperature of the cell to 300°C gave much clearer definition of the bands, but little additional chemical information. It was, moreover, no longer certain that the process occuring was the same as that in the bonding cycle because of the higher temperature, indeed there were suggestions of additional bands in this spectrum.

Then the heated cell was transferred to a Perkin Elmer 598 spectrometer where the signal could be intensified by iterative scanning and the background absorption due to the water and carbon dioxide in the atmosphere could be subtracted electronically. This gave a spectrum with quite sharp and reasonably distinct peaks in the 650-2000 cm^{-1} region. Assignment of these bands proved unexpectedly difficult and only limited conclusions could be drawn.

Undoubtedly this volatile material was of organic, aromatic character and contains a p-substituted phenolic group and there is some evidence of an ether linkage. Thus it could be similar to bis phenol A.

CONCLUSIONS

All the evidence leads to the conclusion that the fully cured composite matrix liberates small amounts of volatile organic material as well as significant amounts of moisture under the curing conditions for a separate adhesive. This is in spite of the fact that the original curing of the composite has been up to 185°C and the curing of the adhesive is only up to 150°C. The spectrum of these volatile materials is consistent with them being very small amounts of material remaining from the original synthesis or possibly slight decomposition products of the composite matrix resin.

Thus there is a source of weakness in these joints which has so far been little explored.

Acknowledgements

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