The Detection of Thin Films of Epoxy Resin on Metal Surfaces

INTRODUCTION

As part of a research program on the effects of the state of cure of epoxy resins on the properties and performance of metal–metal bonds, methods have been sought for the determination of the mode of bond failure in tensile shear tests. Two apparently novel methods have been developed to indicate the presence of very thin adhesive films on adherend surfaces after the joint has failed. The first method involves an iodine staining technique and the second employs the interference colors produced by thin films in polarized light.

The adhesive used in most of this study was diglycidyl ether of bisphenol A (DGEBA) cured with 4,4′-diaminodiphenylmethane (27 parts per hundred parts of resin); these were proprietary materials supplied by Ciba-Geigy (UK) Ltd, AY105 and HT972, respectively. The adherends were 16 SWG aluminum-clad alloy to BSL 73, etched to DTD 915B; joints were 1 in. wide and $^1/_2$ in. overlap, with glue lines in the order of 0.001 in. thick.

EXPERIMENTAL

Iodine Staining

This technique is based on a method commonly employed in chromatographic studies, and a number of variations were tried. In the first of these, broken joints were exposed to iodine vapor at 100°C. The AY 105/HT 972 system gave a blue-green color, but the staining was uneven and the oxide surface on the etched adherends was stained brown.

An acceptable staining method was effected with an aqueous solution of iodine in potassium iodide. The effects of temperature and iodine concentration on the rate of staining were investigated qualitatively. Equivalent intensities of staining were obtained, in 0.1*M* I_2, after 2 min at 40°C or 25 sec at 60°C; these times could be reduced by preheating the joints to the staining temperature. A tenfold increase in iodine concentration reduced the time taken for an equivalent staining intensity by half to two thirds. Staining by this method is fast, uniform, and confined to the resin surface; the oxide surface on the etched adherends is not stained in any way.

Solutions of iodine in organic solvents (trichloroethylene and ethanol) were also found to be effective in staining the resin; e.g., ca. 1*M* iodine in ethanol gives intense staining in 10–20 sec at room temperature. Such solutions are, however, less effective than the aqueous system for staining very thin layers of resin.

Three other reagents have been found effective in giving the same blue-green color; these were chromic acid at 50–60°C, bromine in carbon tetrachloride or in aqueous solutions (from KBr, $KBrO_3$, H_2SO_4) at room temperature, and concentrated nitric acid at 70°C.

A range of other Ciba-Geigy resin-hardener systems which were found to give brown stain with iodine in ethanol were resin DGEBA (AY105 or MY 750) with the following hardeners: a hydroxyalkylated polyamine, HY 956; triethylene tetramine, HY 951; hexahydrophthalic anhydride, HT 907; "nadic" methyl anhydride, HY 906; 2,4,6-tris-(dimethylaminomethyl)phenol, HY 960; and an aminoamide curing agent, HY 953F. A blended epoxy resin, AY 111, and a thiokol-type curing agent, HY 111, also gave a brown stain. Resins cured with 4,4′-diaminodiphenylsulfone, HT 976, only gave a brown stain after prolonged immersion in the staining solution.

The maximum depth of staining in bulk specimens of resin was measured by encapsulating a piece of stained resin, which had been immersed in ca. 1*M* I_2 in ethanol at 60°C for 30 min, in a block of similar unstained material. A flat surface was then ground at right angles to the stained surface. The depth of staining was measured microscopically as 50 μm. Normal staining is 10–20 sec at ca. 20°C. This is found to

give a penetration of 10–20 μm. Riev and Smith[1] measured the depth of staining with osmium tetroxide as ca. 20 μm.

Interference Method

This technique uses interference in polarized light. A beam of polarized light is directed onto the surface of the broken joint at an angle of ca. 45°, with the plane of polarization at 45° to the plane of incidence. The reflected light is viewed through an analyzer aligned parallel with the polarizer. Under these conditions, a thin film of resin on the adherend surface gives rise to interference colors. The color depends on the thickness of the film, and for optically thick films, no color is seen. The technique can be used for any adhesive which is transparent when present as a thin film. Epoxy resin films on a variety of metal adherends have been detected using this method. As expected, the color produced was dependent on the film thickness and independent of the composition of the adherend, although no color has been observed for films on glass adherends.

DISCUSSION

The blue-green stain appears to be specific to those epoxy systems in which 4,4′-diaminodiphenylmethane is used as a hardener, and is also produced by other oxidizing agents (bromine, chromic acid, and nitric acid). No stain is produced when the structurally similar 4,4′-diaminodiphenylsulfone is used, nor is the stain produced with the separate components. These facts suggest that the color is produced by oxidation of the cured system. The possible sites of oxidation are the hydroxy groups in the resin, the methylene bridges in the hardener, and the secondary and tertiary amino groups. The first of these involves no change in the conjugation of the system, and in the second, conjugation is sterically hindered, but may well be of importance since the color is not observed with other amines.

In addition, the system possesses some similarities to the diphenylmethane and triphenylmethane dyes such as malachite green. It is possible that, on oxidation, the methylene group of one diphenylmethane chain segment is linked to the 3-position of another diphenylmethane segment or to the 3-position of one of the rings in the DGEBA. Either of these would allow the necessary conjugation, in an ionic structure, to produce the observed color.

However, the brown color obtained with a fairly wide range of other cured epoxy resin systems is also a valuable technique for detecting very thin films of residual adhesive resins.

The second technique, use of polarized light, relies mainly on one physical property of the film, its thinness. This method is, therefore, of more general use than the staining technique and can be used on almost any metallic adherend.

Reference

1. C. K. Riew and R. W. Smith, *J. Polym. Sci.*, **9A**, 2739 (1971).

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