Further studies on the effect of carriers on the performance of aluminium alloy joints bonded with an epoxide polyamide adhesive

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(*Received* 6 *August* 1980)

INTRODUCTION

We have previously reported[1] the effect of exposure to warm moist air (50°C and 100% r.h.) for up to 1000 h on the strengths of double lap joints of aluminium alloy (BS3L73) bonded with adhesives based on American Cyanamid FM 1000. We now report the results of longer exposure periods up to 10 000 h. Also reported is the use of phosphoric acid anodizing as an alternative metal surface pretreatment to chromic acid etching. All experimental methods employed have been described elsewhere[1,2]. The adhesives used were: FM 1000 (a film adhesive without carrier); FM 1000/OKN (contained an open knitted nylon carrier); FM 1000/EP15 (contained a close knitted nylon carrier).

RESULTS AND DISCUSSION

Durability of double lap joints with chromic acid etched adherends

The strengths of double lap joints with chromic acid etched adherends are shown against exposure time in *Figure* 1. The results for both carried and uncarried adhesives are given and it can be seen that there is no significant difference between the two sets of points. Experimental errors were usually less than the size of the symbols in the Figure. Some of the joints which were stressed to 20% of the mean initial dry strength failed during exposure. FM 1000/OKN failed after 3420, 3603 and 3741 h and FM 1000 joints failed after 3252, 3265, 3465, 3667 and 3991 h. Those joints which remained intact were then destructively tested and found to have strengths close to the locus of *Figure* 1. (These are indicated with an asterisk.) In this test a string of 5 joints was loaded to 8 kN (FM 1000) and 7 kN (FM 1000/OKN). When three of the joints had failed the remaining two joints were tested. Their strengths were found to be close to those of unstressed joints exposed for 3500 h, i.e. 23 and 16 kN, respectively. The parameters which may account for such a large dissimilarity in strength are firstly temperature and secondly rate of stress. In the environmental chamber failure was at 50°C and zero rate of stress, whereas the joints removed from the chamber were tested at 20°C and a rate of stress of 10 kN min^{-1}.

Moisture altered the failure mode of the unsupported FM 1000 from apparent interfacial failure with tearing of the aluminium cladding to progressively larger amounts of cohesive failure. The tensile moduli of cured films of FM 1000 have been found to be greatly reduced by water[3,4]. Thus when adhesive joints of FM 1000 were subjected to high humidity, cohesive failure in the resin occurred. Prolonged exposure to high humidity (5000–10 000 h) caused a further change in the failure mode of joints bonded with FM 1000 and FM 1000/OKN. The failure appeared to be associated with a weakening of the oxide layer. Patches of aluminium were visible to the naked eye on the opposite fracture surface. The strength of the joints had declined to 20% of the original dry strength after 10 000 h exposure.

Some workers have suggested[5-8] that changes in the oxide layer are the cause of the deterioration in the strength of adhesive joints. Water may diffuse through the resin to the interface and interact with the oxide causing a slow hydration which increases the oxide thickness due to the greater molar volume of the hydrate. In this manner, a type of weak boundary layer is created and when stress is applied, failure occurs through the hydrated oxide. This mechanism accounts for the observed incomplete recovery of strength of drying[1], since water removed would result in a cracked oxide[7]. Evidence in support of this mechanism has recently been provided by surface spectroscopy on failed joints[9].

We have previously demonstrated a linear relationship between joint strength and the water uptake of lap joints. This was demonstrated using the film adhesive BSL 312[2], and an adhesive based on the diglycidyl ether of bisphenol-A and di-(1-aminopropyl-3-ethoxy)ether[10].

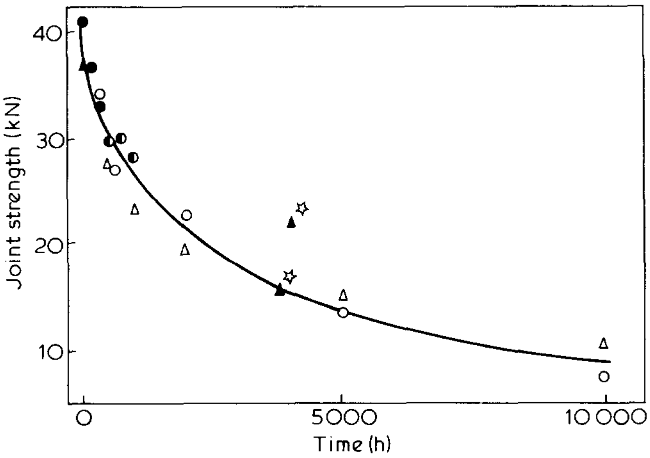

Figure 1 Dependence of joint strength on exposure time for double lap joints with chromic acid etched adherends. ○, ●, FM 1000 adhesive; △, ▲, FM 1000/OKN; open symbols = unstressed joints; filled symbols = joints stressed to 20% of dry strength. Asterisk denotes strengths of joints which remained intact after other members of its group had failed under static stress

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0032-3861/80/1477-02$02.00

This linear relationship holds for FM 1000 up to fractional uptake of water of about 0.9, then a distinct fall from the straight line is evident (*Figure* 2). At lower levels of water uptake the main effect of water is to plasticize the resin and lower its cohesive strength, but at longer times the hydration of the oxide layer, which has been mentioned above, weakens the oxide layer and causes this fall from linearity. Fractional uptake of water was calculated by a method described previously[10], using a value of 3.4 $\times 10^{-12}$ m^2 s^{-1} for the diffusion coefficient.

Phosphoric acid anodize surface pretreatment

Strengths up to 2000 h exposure for phosphoric acid anodized joints are shown in *Figure* 3. These points show the carried joints to be slightly weaker than the uncarried ones, but otherwise these points are in general agreement with the locus of *Figure* 1. Phosphoric acid anodizing seems to offer no improvement in durability with FM 1000 but this result supports our assertion made above from the evidence of increasing cohesive failure up to 5000 h, that in this period, plasticization of this adhesive by entering water is the most important factor. In contrast joints prepared with the modified epoxide adhesive BSL 312 after treatment by phosphoric acid anodizing were found to be significantly more durable[2].

There is evidence[11] that phosphoric acid anodizing produces a more durable oxide layer, but our results for chromic acid etched adherends bonded with this nylon–epoxide adhesive would imply that the advantages of a more durable oxide would not be evident for exposures less than 5000 h. After this time the water which has entered the bondline by diffusion starts to attack the oxide produced by etching.

An additional factor which may be responsible in part for the differing durability of BSL 312 and FM 1000 after phosphoric acid anodising is the relationship between viscosity and temperature for the two adhesives. On heating BSL 312 film adhesive the viscosity of the resin decreases rapidly. FM 1000, however, remains in film form until 150°C when melting occurs and curing commences. It has been observed[12] that nylon epoxide film adhesives may cure before melting if too slow a heat-up rate is used. This is particularly significant with phosphoric acid anodized aluminium due to the morphology of the oxide. Venables *et al.*[13] have studied the structure of the oxide by transmission electron microscopy in the scanning mode and found it consisted of porous columns with 'whisker-like' protrusions. The oxide is about 600 nm thick on a clad aluminium alloy[14]. It is highly probable that in the case of FM 1000 curing occurs before these deep pores have been thoroughly wetted by the adhesive.

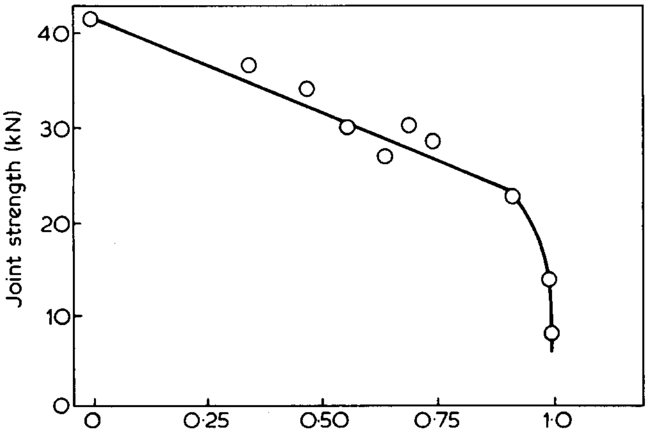

Figure 2 Dependence of joint strength upon water content. (FM 1000 with chromic acid etched adherends)

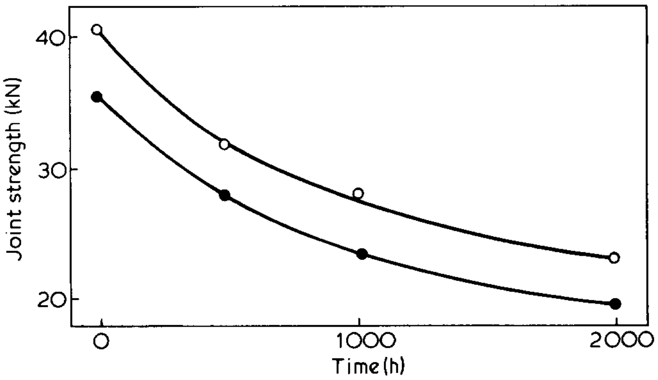

Figure 3 Dependence of joint strength on exposure time for double lap joints with phosphoric acid anodized adherends: ○, FM 1000; ●, FM 1000/OKN

Schwartz[15] has reported that another 175°C curing epoxide film adhesive exhibited similar durability when treated by phosphoric acid anodizing or chromic acid etching. This was later ascribed to the rubber-based primer rather than the adhesive[16]. The porous oxide was described as acting like a molecular sieve in that lower molecular weight rubber molecules penetrated the pores but molecules of higher molecular weight remained at the surface of the oxide. In this manner a type of weak boundary layer was created and premature failure occurred.

CONCLUSIONS

(1) When open knitted carriers are incorporated into the adhesive FM 1000, there is no effect on the strength (measured at a finite strain rate) of joints even when they are exposed to hot humid air for 1000 h.

(2) The application of a 20% stress to joints similarly has no effect for exposure times up to 1000 h. However, both uncarried and carried adhesives based on FM 1000 failed under this stress level after approximately 3500 h.

(3) Up to about 5000 h cohesive failure dominates but is increasingly replaced by interfacial failure at longer times as the metal oxide is hydrated. At lower times strength is linearly related to water uptake.

(4) Up to 5000 h phosphoric acid anodizing offers no advantages over chromic acid etching as a surface pretreatment for the substrate–adhesive system used.

ACKNOWLEDGMENTS

The authors thank the Procurement Executive, Ministry of Defence for the financial support given to this programme. They also thank the following for their support and interest, Dr B. M. Parker, Dr A. K. Green, Dr J. L. Cotter.

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Self-diffusion of short-chain polystyrenes in deuterochloroform solution

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(*Received* 14 *June* 1980)

This report details investigations concerning determination of the translational self-diffusion coefficients for monodisperse short-chain polystyrenes ($M = 510$, 1010, and 3300, $\bar{M}_w/\bar{M}_n \leqslant 1.11$) in deuterochloroform (99.8%) at 25°C within the polymer weight fraction interval $\omega_{PS} = 0.13$–0.61, through proton (99.6 MHz) pulsed magnetic field gradient spin–echo nuclear magnetic resonance measurements. The technique employed has been described elsewhere[1,2] and uses a pulsed field gradient, generated through the software-controlled spectrometer (JEOL FX-100) homogeneity-spoiling (homospoil) coils. Fourier transformation of the spin–echoes allows determination of the D and T_2 values from the signal attenuation with increasing gradient duration, for an observed individual proton spin group in the molecule.

The polystyrene samples, obtained from Polymer Laboratories Ltd, and used as received, were chain-terminated with an n-butyl group. This terminal methylene chain group provided an ideal proton signal with relatively long values of T_2 and, unlike the aromatic protons, did not display disturbing J modulation effects upon Fourier transformation of the accumulated spin–echoes. The T_2 values, measured in the same manner as in the diffusion experiment albeit with the gradient switched-off, were of the order of 120–160 ms and decreased with molecular weight. No drastic changes in T_2 could be observed around the critical concentration, c^*, for coil overlap (evaluated earlier[3] to be approximately $\omega_{PS} = 0.43$, 0.33 and 0.19 for molecular weights 510, 1010, and 3300, respectively).

As the diffusion experiment measures spatial proton displacements during a time duration of roughly 0.1 s, which corresponds to a traversed distance of approximately 5×10^4 Å (assuming $D \sim 10^{-10}\ \mathrm{m}^2\,\mathrm{s}^{-1}$) or about 100–500 times the chain diameters, chain segment reorientational displacements and overall chain rotation should not contribute and the measured quantity should indeed by the self-diffusion coefficient, similar to earlier arguments presented elsewhere[4].

For these short-chain polystyrenes, well below the critical molecular weight for the occurrence of intramolecular entanglements in solution[5], the self-diffusion coefficients were found to decrease rapidly with increasing concentration and molecular weight (*Figure* 1), such that log D decreased linearly with increasing concentration, the slopes increasing with molecular weight (*Figure* 2). These results are in qualitative agreement with earlier n.m.r. pulsed-gradient spin–echo studies[4] on short-chain ($\bar{M}_n = 590$) poly(ethylene oxide) and poly(dimethyl siloxanes) in dilute to concentrated solutions and on concentrated polystyrene solutions in toluene-d_8 [6] and with Rayleigh light-scattered linewidth measurements on low molecular weight polystyrenes in dilute solutions[7].

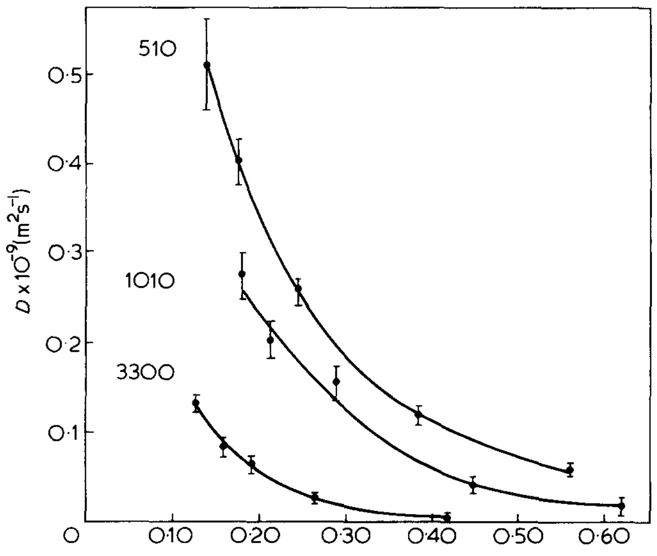

Figure 1 Self-diffusion coefficients for short-chain polystyrenes (molecular weights 510, 1010 and 3300) in deuterochloroform at 25°C as a function of polymer weight fraction

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