The Effect of Possible Contaminants on the Adhesion Properties of Thermosetting Resins Used in Repair Situations.

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Abstract

The effects of possible contaminants (typical materials found in composite repair environments within the aircraft industry) on an epoxy adhesive - CFRP adherend interface during bonding were investigated employing a static mechanical technique. The chemical system studied was Cyanamid's FM 300M film adhesive. The contaminants examined were Skydrol - a hydraulic fluid, Ardrox - a degreasing agent, and Cured Grit. The adhesive strength properties were determined in shear by tension loading of single-lap-joint laminated assemblies. The effects of the presence of the various contaminants were investigated by observing variations in the load at failure, thus allowing any changes in the 'physics' of the joint to be noted. The results indicated that the adhesive was capable of absorbing the bulk of the contaminant and of displacing the adsorbed contaminant from the adherend surface.
Keywords: Bonding, interface, epoxies, contamination, joint, adhesive strength.

Introduction

Thermosets based on crosslinked epoxy resins are used extensively as matrix materials in high performance fibrous composites prepared from prepregs. Within the aircraft industry they also find application as adhesives for assembling and repairing these composite structures (1-3).

The chemical structure, purity, functionality, and composition of these matrix resins, as well as the extent of reaction, influence the final network structure and hence the bulk properties of the cured thermoset (4). Small variations in the formulation or processing conditions, which effect cure, can dramatically alter the properties of the final network.

Composite aircraft components, like their metal counter-parts, are subject to damage and subsequent repair within a workshop environment is not always feasible. A potential difficulty encountered in repair under non-ideal conditions is ensuring effective surface pretreatment. Skydrol - a hydraulic fluid used extensively within the aircraft industry, Ardrox - a degreasing agent used during composite repair, and Cured Grit resulting from the cleaning of the damaged surface may each be present during the cure process of the epoxy repair adhesive, hence altering the properties of the end-repair.

In order to form a strong bond with a contaminated composite surface the epoxy adhesive must be capable of performing two separate tasks. Firstly, the adhesive should be capable of absorbing the majority of the contaminant and of diffusing towards the composite surface. Secondly, having absorbed the bulk of the contaminant, the adhesive should be capable of displacing the contaminant adsorbed directly onto the substrate. The effects of the absorbed contaminants on the chemistry of cure, determined employing calorimetric and rheological techniques have previously been discussed (5). The focus of the present study is to investigate the effect that adsorbed contaminants may have on the interfacial region formed by the interaction of an epoxy/amine adhesive and a composite substrate.

Adhesion is a phenomenon which exists within a few molecular layers of the contacting surfaces. The presence of contaminants in this interfacial region can greatly influence the formation of substrate surfaces, which, would have been conducive to efficient intermolecular interactions resulting in both initial joint strength and longevity in the intended service environment. The adhesive strength properties of a commercial epoxy adhesive were estimated in shear by tension loading of single-lap-joint laminated assemblies. The load at failure was determined in accordance with ASTM D-3165. The effects of the adsorbed contaminants on joint strength were characterised by observing variations in the load to failure while the modes of failure were employed to elucidate upon the interaction of the contaminants with both the adherend and the adhesive.

Experimental

I. Materials

The resin system chosen for this study was Cyanamid's FM 300M film adhesive, a system specified in the Airbus A 320 and Boeing structural repair manuals. The composite laminate adherends were fabricated from Ciba Geigy T-300/914C prepreg, layed up in a $(0,90)_{4S}$ orientation. To maximise joint strength, the 0° plies (parallel to the load) were placed on the outside of the adherends, i.e., next to the adhesive layer. Test specimen geometries based on Section 7 of ASTM D 3165 and illustrated in Figure I, were machined employing conventional techniques, the length of overlap being 12.7mm.

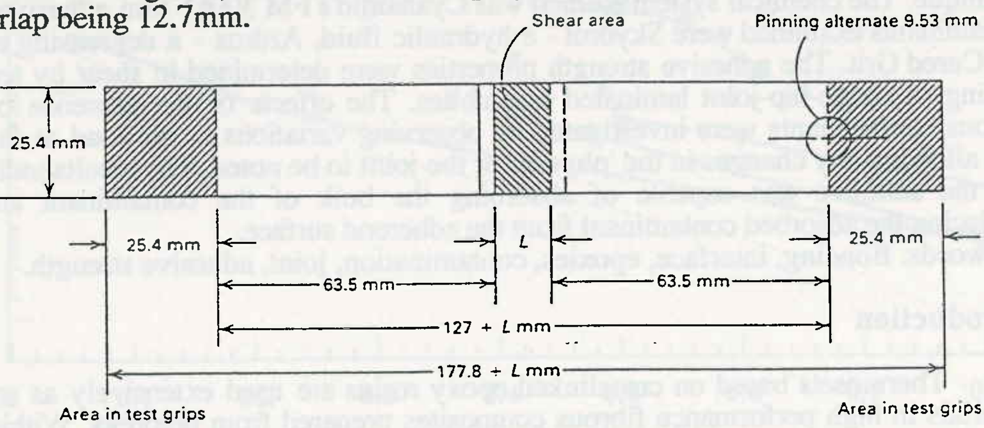


Figure I. Test specimen geometries.

II. Sample preparation

The composite surfaces were prepared for bonding via the following steps:

- washing of the substrate surface with a 2% aqueous solution of detergent at 50°C,
- thoroughly rinsing in tap water, then immersing in distilled water,
- drying in forced air oven at 60°C for 30 minutes,
- abrading bonding area with 600 grit adhesive paper,
- cleaning of abraded area,
- swabbing abraded area with acetone and wet, clean gauge,
- drying in forced air oven at 100°C for 60 minutes,
- further drying in forced air oven at 60°C for 48 hours.

The above cleaning procedures produced surfaces that were fully wetted out by water indicating the formation of clean, hydrophilic surfaces. The substrates were subsequently contaminated by wiping a gauge saturated with either Skydrol or Ardrox along the bonding surface of the substrate. This procedure left a clearly visible contaminant film on the adherend. In the case of the Cured Grit, the last three steps in the cleaning procedure were ignored thus leaving a layer of debris on the surface. The substrates were subsequently bonded together, by curing the film adhesive at 175°C for 60 minutes.

III. Methods

The adhesive strengths were determined in shear by tension loading of single-lap-joint assemblies, in accordance with ASTM D 3165-91 (6), on an Instron 4302 Static Testing system at ambient temperature. Modes of failure of the broken joints were classified as:

- Failure in the composite - C,
- Failure in the adhesive/composite interface - I,
- Cohesive failure in the adhesive - A.

In the case of more than one mode of failure occurring, each type was listed.

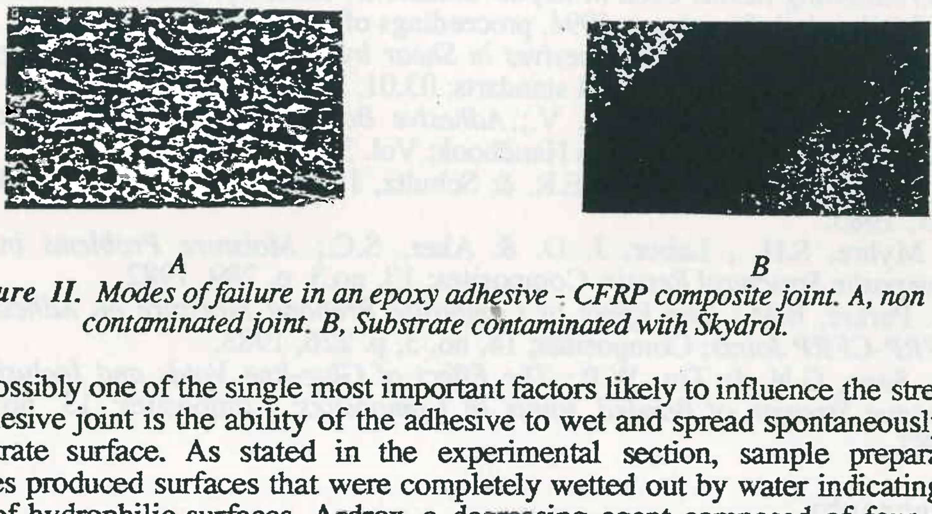
Results and Discussion

The use of conventional surface preparation procedures is considered crucial in ensuring optimum adhesive and maximum environmental resistance of adhesively bonded CFRP - CFRP substrates (7). Contaminants present during the bonding process are generally viewed as having detrimental effects on the physical properties of the resulting joint. Outlined in Table I are the effects of Skydrol, Ardrox and Cured Grit on joint strengths and their respective modes of failure. Initially, one may view these results with scepticism as they appear to suggest that the adhesive is capable of forming strong adhesive bonds with contaminated surfaces. Debski *et al* (8) have shown that it is thermodynamically possible for a model epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) to displace an apolar standard ASTM 3 mineral oil from a metal surface. They also showed that an epoxy resin cured with 6% dicyandiamide could absorb the oil from the metal surface but that the oil could inhibit crosslinking reactions and also plasticise the adhesive. In view of these findings, an explanation of the increased strength of Skydrol contaminated systems may be proposed.

Resin System	Load at failure (kN)	Mode of failure
Reference	2.4±0.1	A
+ Skydrol cont.	3.0±0.2	A & C
+ Ardrox cont	3.7±0.3	A & C
+ Cured Grit cont	3.1±0.3	C

Table I. Joint strengths for the various formulations and their modes of failure.

During cure the adhesive, having absorbed the bulk of the contaminant successfully, displaces the Skydrol adsorbed directly onto the substrate and forms a strong bond. Incorporation of Skydrol within an epichlorohydrin derived epoxy formulation has been found, in previous work (5), to antiplasticise the resin system. On a macro scale, antiplasticisation translates into an increase in glassy modulus meaning that in this glassy temperature range (T_g >> ambient) the contaminant can accommodate a greater load prior to failure. This increase in modulus of the adhesive accompanied by efficient intermolecular interactions also shifted, in part, the mode of failure away from adhesive cohesion and into the the composite (see Figure II). Of greater significance here is the lack of adherend/adhesive interface failure generally associated with contaminated substrate surfaces. This further suggests that Skydrol has an affinity for the epoxy adhesive and does not interfere with the bonding of the adhesive to the laminate surface.



A B

Figure II. Modes of failure in an epoxy adhesive - CFRP composite joint. A, non contaminated joint. B, Substrate contaminated with Skydrol.

Possibly one of the single most important factors likely to influence the strength of an adhesive joint is the ability of the adhesive to wet and spread spontaneously on the substrate surface. As stated in the experimental section, sample preparation procedures produced surfaces that were completely wetted out by water indicating the creation of hydrophilic surfaces. Ardrox, a degreasing agent composed of four parts water (by weight) increased the bond strength of the adhesive. It is proposed that Ardrox improved the ability of the adhesive to wet and spread on the substrate surface.

The lack of any void formation at the interface, is however, surprising. Again, the mode of failure shifted, to a small degree, into the composite.

The final contaminant examined was Cured Grit resulting from abrasion of the bonding surface. Its presence on the adherend surface may increase the bond area and mechanical interlock and these factors may create the environment which promoted increased bond strength.

Absorbed moisture in the laminate has been found to be a major problem in the bonded repair of composite structures (9,10) and to be one of the causes of voiding in the bondlines (11). This is due to the entrapment of desorbed moisture in the adhesive. In the current study however, the contaminants, prior to bonding were concentrated along the laminate surface, and hence, were not required to diffuse out of the substrate during the cure cycle. It is thus feasable that, any volatile components given of by either Skydrol or Ardrox, evaporate and diffuse away from the joint prior to being entrapped by the constraints imposed by gelation of the growing three dimensional network. Subsequently, no interference with the bonding of the adhesive to the laminate surface would occur.

Conclusions

Cyanamid's FM 300M epoxy film adhesive was capable of absorbing, and subsequently displacing the adsorbed contaminants from a CFRP substrate to produce joints with optimum strengths. The results also indicate that substrate/adhesive interaction combined with the nature of the absorbed contaminant will have a marked effect on joint strength.

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Biography

Kilian O'Byrne is a graduate of Kevin St. College of Tech., Dublin, having received his BSc in Applied Science (Chemistry/Physics option) from Trinity College. He is currently studying towards the award of PhD under the guidance of Prof. Martin

Buggy. He is a member of the Materials Ireland, Polymer and Composite Research Unit based at the University of Limerick. His work is concerned with the effects of possible contaminants on the chemistry of cure and the resulting adhesion properties of thermosetting resins employed in repair situations.