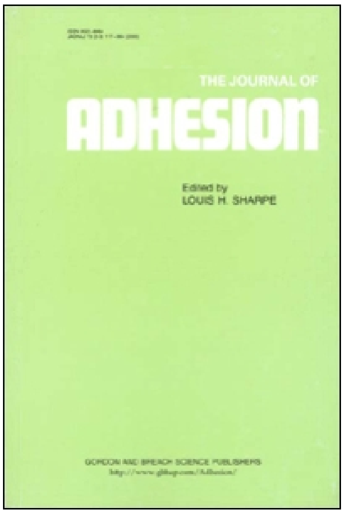

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Moisture Uptake by Some Uncured Adhesive Films

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NOTE

Moisture Uptake by Some Uncured Adhesive Films

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KEY WORDS Gas chromatography; moisture uptake; flow; tensile-shear strength; uncured epoxy film adhesive; uncured graphite-epoxy composite.

INTRODUCTION

The uptake of moisture by epoxy-based adhesives and fibre reinforced composites after cure has been the topic of many studies. The extent of moisture uptake by uncured adhesive films and composite prepregs, and the effect which this has on the performance of such systems after cure, has received much less attention. It is, nonetheless, recognised as an important consideration and most aerospace lay up facilities include controlled humidity conditions.

Previously published results for moisture uptake were obtained using gravimetric or Karl Fischer analyses or the Du Pont Moisture Evolution Analyser. These methods suffer from certain disadvantages: gravimetric analysis is not specific to moisture gain or loss, the traditional Karl Fischer reagent has a very limited life and an unpleasant odour of pyridine while the Moisture Evolution Analy-

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ser requires purchase of a specific, relatively expensive instrument. Although a gas chromatography (GC) method has been mentioned[1] for moisture determination, no detailed data on its use seem to have been published. This Note presents data obtained by GC, on the rate and extent of moisture uptake by a number of uncured film adhesives, together with a brief indication of the effect on performance of certain systems.

EXPERIMENTAL

The procedure developed for this work was based broadly on that of McDonnell Douglas.[1] A Varian 1400 GC instrument, fitted with a thermal conductivity detector, was used. Instrumental parameters were as follows: sample column 1.5 m × 3.2 mm packed with Porapak QS 80/100 mesh, reference 550 mm restrictor column, sample column temperature 150°C, carrier gas helium at flow rates of 26 and 11 ml/min in sample and reference columns, respectively. The solvent was dichloromethane.

The equipment was calibrated regularly with solutions of water in dry dichloromethane in the concentration range 0 to 1.32 g/l, the upper limit being effectively set by the solubility of water in the solvent.

Some problems were encountered with column blockages after several hundred injections, probably due to an accumulation of high molecular weight components. This necessitated removal of the first few cms of column packing and its replacement with new material. It was also found to be necessary to replace the septa after about 30 injections to minimise leakages.

Four film adhesives and one carbon-fibre composite prepreg were examined. Details of these materials are given in Table 1. At the commencement of this study all of the materials had been in freezer storage at −18°C for some months. Samples were held, with the protective film removed from one side, under controlled humidities of 54% and 92% RH at 12°C, to minimise resin advancement. Material was withdrawn at appropriate intervals over 35 days, dissolved in dry dichloromethane and the moisture content determined as the average of three replicates. Agreeement between replicates was generally very good.

TABLE 1
Materials

Name	Manufacturer	Type	Weight Kg/m^2	Recommended cure temperature °C
FM 1000	American Cyanamid	Nylon-Epoxy Adhesive (unsupported)	0.30	177
FM 300	American Cyanamid	Rubber-Modified Epoxy (supported)	0.50	177
AF 163-2K	3M	Rubber-Modified Epoxy (supported)	0.15	121
AF 126	3M	Rubber-Modified Epoxy (supported)	0.30	121
AS/3501-6	Hercules	Epoxy-based Carbon-fibre Composite Prepreg	0.30	177

Samples of the humidity aged adhesives were also used for flow measurements and for preparation of Al–Al single lap joints using the manufacturer's recommended cure cycle. Procedures for this have been described previously.[2]

RESULTS AND DISCUSSION

Moisture uptake

The rate and extent of moisture uptake at 92 and 54% RH at 12°C are shown in Figures 1 and 2. As expected, the nylon-epoxy system FM 1000 absorbed the most (about 6% in the high humidity atmosphere). The two more recent systems, AF 163 and FM 300, claimed to be moisture resistant, absorbed much less (around 1%), while the older AF 126 lay between these extremes (about 2.5%). The carbon fibre composite AS/3501-6 absorbed about 1% moisture based on the overall mass (or over 3% based on the resin content). The extent of moisture uptake at 54% RH was about 2.5 times less than at 92%.

Several authors have reported on moisture levels in uncured, unidentified, aircraft adhesives using Karl Fischer or gravimetric analyses.[3,4] Values ranged up to about 1% with a difference of about 3 fold between 50 and 95% RH conditions. "As received" moisture content was about 0.15%, which is somewhat less than the

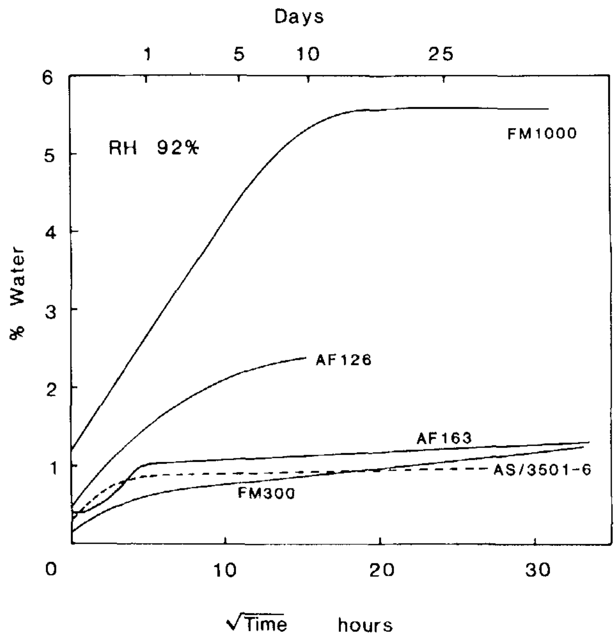

FIGURE 1 Water uptake during exposure at 12°C and 92% RH.

initial values for the "moisture resistant" adhesives in the present work.[3]

Dodiuk *et al.*[5] examined the mass changes during drying and humidifying cycles for various adhesives. For the "as received" materials mass losses on drying of around 0.4% were reported for FM 73 and FM 300 K, about 0.8% for AF 126 and around 0.2% for Ciba-Geigy's Redux 319. Mass losses may not exactly reflect moisture content since not all moisture may be removable under the conditions used and loss of other volatiles, such as traces of solvent, would be included.

Pike *et al.*[6] found, by Karl Fischer analyses, that Hysol's EA 9649 "as received" contained about 0.5% moisture. After immersion for 4 hrs in water the unsupported version contained 3.5% moisture and the supported form 1.6%.

Moisture uptake of the carbon fibre prepregs AS/3501-6 and T300/5208 has been the subject of a number of studies.[7–10]

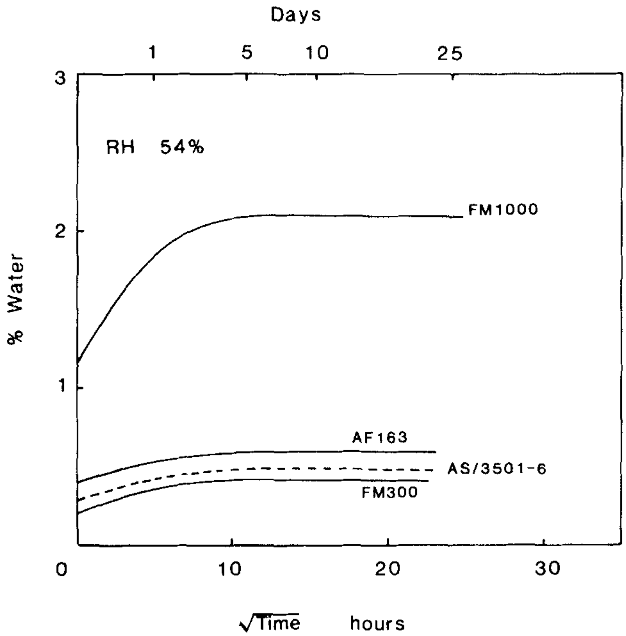

FIGURE 2 Water uptake during exposure at 12°C and 54% RH.

Reported values for the amount of moisture taken up vary but are generally around 0.8% for exposure at ambient temperature to 90% RH or greater, as determined by mass changes or the Du Pont Moisture Evolution Analyser. Part of the discrepancy in results between various workers probably arises from the length of the exposure to the high humidity conditions, that is, equilibrium had not always been reached. Values of the "as received" moisture content for AS/3501-6 of around 0.25% have been noted.[8]

Thus, the values reported here, determined by the GC method, are broadly similar to previously reported values determined by other methods.

To gain an impression of the ease of moisture removal, samples of FM 300, after 10 days at 92% RH, were placed over silica gel in an evacuated desiccator. After 1 h the moisture content had fallen from 1.0% to 0.66%. After 16 h the water content was about 0.1%. It may be that moisture is relatively easy to remove down to about the 0.1% level but that the remaining moisture is held rather more tenaciously.

Effect on performance

Determinations of the flow during cure were made for AF 126, FM 300 and AF 163 after 14, 23 and 22 days, respectively, at 12°C and 92% RH. Compared with control samples FM 300 and AF 163 showed virtually no change while the flow of AF 126 decreased from about 5% to under 2%. Although this latter adhesive had taken up more than twice as much moisture as the other two, the change in flow is of the same order as would be anticipated from thermal ageing alone.

Conflicting reports have been made on the effect of prior exposure to high humidities on adhesive flow during cure. An increase in the minimum viscosity reached by a resin during a standardised heat-up cycle has been reported for Narmco 5208[7] and for an unspecified, 177°C curing adhesive.[3] This would suggest an effect on flow during cure similar to that of resin advancement, with the distinction that the effect can be removed by a drying cycle.[3,7] Some authors[7] also reported a reduction in the initial viscosity which is not evident in the data of others.[3] Substantial increases in flow have been reported[4,6] for some adhesives and also a significant reduction for another.[3] Clearly, each formulation has to be examined separately.

Tensile-shear strengths of Al–Al single lap joints were measured for FM 300 and AF 163 using adhesive aged at 92% RH for various times up to 23 days. Tests were conducted at ambient temperature and at 150°C for FM 300 and 113°C for AF 163. Both adhesives were effectively unchanged in their room temperature tensile-shear strength but showed a reduction of around 20–30% in the elevated temperature values. Most of this reduction occurred in the first 100 hrs of humidity exposure, which corresponds with the time over which most of the moisture uptake occurred.

Paradis[11] reported a drastic reduction in 120°C tensile-shear strength of FM 73 and EA 9628 after prolonged prebond exposure to 80% RH. Dodiuk *et al.*[12] reported a gain of about 20% in lap-shear strength at 105°C for FM 300 after a drying cycle during which a weight loss of about 0.3% occurred in the adhesive. This is broadly similar to the effects noted here. A more substantial strength gain was reported for FM 73 under the same conditions.[12] Pike *et al.*[6] found no effect of moisture content on the room temperature tensile-shear strength of EA 9649. Kibler and Creasy reported[3] a reduction of about 10% in lap shear strength at ambient temperature and about 15% reduction at 90°C after the adhesive was aged at 75% RH.

A severe reduction in the low temperature peel strength with increasing moisture content has been reported for an unspecified 350°F curing film adhesive. AF 163 was specially formulated to overcome this problem.[13]

Absorbed moisture may affect the cure chemistry[14] and result in substantial changes in adhesive strength, especially at elevated temperatures. Again, it can be anticipated that the magnitude of such effects would depend on the formulation and thus each system would need to be considered separately.

CONCLUSIONS

Values of the extent of moisture uptake, as determined by GC, agree well with earlier determinations using other methods.

The moisture uptake of FM 300 and AF 163, formulated to give improved moisture resistance, is substantially less than a number of older systems examined. The effect of moisture on performance during and after cure for these two adhesives, as measured by flow and lap-shear tests, is relatively small.

Acknowledgement

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