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Testing Epoxy Composite Surfaces for Bondability :

Brenda M. Parker*
Materials and Structures Department, Royal Aerospace Establishment, Farnborough, Hants GU14 6TD, UK

Rex M. Waghorne
Fulmer Research, Stoke Poges, Bucks UK

Composite surfaces before and after pretreatment for adhesive bonding have been examined by x-ray pbotoelectron spectroscopy (XPS) and the extent of transfer of release agents or other contaminants from release agents, which also were analysed by XPS, was estimated. Composite surfaces were examined also by optically stimulated electron emission (OSEE). Surface anlyses were correlated with the strength of adhesive bonded joints. OSEE shows promise as a non-destructive method for determining the bondability of epoxy resin matrix composites.

INTRODUCTION

If a fiber-reinforced composite structure is to be assembled by adhesive bonding, it is necessary to have some assurance that a good bond will be formed. When bonding metals (particularly aluminum) it is relatively easy to obtain good initial bond strength but less easy to ensure durability in hot and humid conditions. With epoxy matrix carbon fiber composite, once a good initial bond to an epoxy adhesive has been formed there is no subsequent loss of strength due to degradation of the adhesive-composite bond:l the problem lies in ensuring a 'clean' surface initially.

At present, there does not seem to be any agreed method of determining the suitability of a surface for bonding, except coupon testing, i.e. making and testing joints of the surfaces to be used in the structure. Several methods of testing surfaces without bonding are avail- able. X-ray photoelectron spectroscopy (XPS) can provide detailed chemical information on the nature of the surface, but requires a sample of the surface to be examined under high vacuum. The water break test2 is quick and easy and will give a yes/no answer on a constant surface, but it is not easy when dealing with an unknown surface. A third method, optically stimulated electron emission (OSEE), 4appears to offer advantages as it is non-destructive and does not require a high vacuum. However, it is not well characterized yet as a method for estimating bondability. In the work reported here, results from XPS and OSEE examinations are compared with each other and with bonded joint strengths.

EXPERIMENTAL

Materials

Carbon fiber-reinforced composite with epoxy resin matrix (Ciba Geigy 914C) was cured and post cured at 180EC against a large number of release agents. These included coated and un-coated nylon and glass cloths (coded N and G, respectively), release films (code F), elastomer sheets (code S) and mould release sprays and liquids (code R), which were baked onto aluminium foil to simulate a metal mould. The composite surfaces obtained on removal of release cloths, etc. were either left untreated or treated by hand abrasion with an abra-sive cloth or by blasting with dry alumina grit. The level of treatment by grit blasting was varied by passing the grit-blasting gun across the composite surface a different number of times. The 'standard' number of passes was three.

X-ray photoelectron spectroscopy

The release agents were analysed by XPS using an AEI/KRATOS ES 200B electron spectrometer. Samples were examined under a residual pressure of ~10^{-8} Torr, using an Al K% incident x-ray beam. Peak binding energies were corrected to the major C ls (C—C, C—H) component at 285 eV, or 292 eV for C—F_2. The spectra were resolved using a DuPont 310 curve analyser. Where possible, the types of atomic bonding relating to the electron bonding energies are given. These are not always unique, especially for oxygen, and are highly dependent on the accuracy of curve resolution. The intensity data were corrected by a series of sensitivity factors established previously from results for standard compounds. The approximate atomic composition of each surface was calculated from the corrected intensity data. Untreated and treated composite surfaces were examined also by XPS, as were samples of cast matrix resin and delaminated composite. The effect of varying the intensity of grit blasting was determined also for surfaces molded against PTFE-coated glass cloth.

Optically stimulated electron emission

Composite surfaces only were examined by optically stimulated electron emission (OSEE) using a PATSCAN instrument consisting of an OP1010 detector with a 0.2 mm diameter probe (settings of 7

On probe and x 10 gain) and recorded using Series 1004 software. Essentially, a beam of UV light is shone vertically onto the surface being examined and the returning photoelectrons are counted. Measurements are taken in a grid pattern over the surface. The OSEE signal was recorded on a scale of 0-10.

Adhesive-bonded joints

The quality of adhesive-bonded joint that could be obtained for selected surfaces was tested by preparing single overlap and floating roller peel joints using a two-part paste epoxy adhesive cured for 1 h at 60EC. After testing, failure surfaces were examined visually; looking especially to see whether failure was between the adhesive and the composite surface.

RESULTS AND DISCUSSION

Composition of release agents

Four samples of matrix resin (clean fractured surface) and one of delaminated composite were analysed. Compositions and peak positions were consistent and the averages are given in Table 1. All bond types, except those due to silicon, were expected from the compounds used to make the matrix resin The prepreg from which the composite is made is supplied with plastic film on one side and a coated backing paper on the other. XPS analysis showed that there was silicon on the side of the film that had been next to the backing paper but not on the side that had been next to the plastic film. From this, it was concluded that the backing paper was silicone coated, and that the coating could be transferred to the uncured epoxy surface. Five polytetrafluoroethylene (PTFE)-coated glass cloths, two release sprays and four release films were analysed: the latter agents had very similar compositions to the glass cloths. The average compositions are given in Table 2. The release agents are as expected within the variability $(\text{—CF}_2\text{—})_n$ with small amounts of extra carbon, could be attributable to environmental contamination, and of oxygen, which might be adsorbed onto the polymer surface. One glass cloth (G7A) and one nylon cloth (N8) were found to be coated partly with a fluorinated compound. As the ratio of C—F_2 to F—C was 1:2 in both cases, the coatings were assumed to be PTFE. Relative to the composition of PTFE found from other fluorinated release agents, the coverage of cloth by PTFE was 78% for G7A and 52% for N8.

Six silicone elastomer sheets were analysed. Excluding catalysts, their compositions were very similar. One release spray and its liquid version had the same composition. The average analysis is given in Table 2. This gives a C/O/Si atomic ratio of 4: 3 :2. The atomic composition of linear dimethylsiloxane polymer $[\text{—O—Si(Me)}_2\text{—}]_n$ would give a C/O/Si ratio of 2: 1: 1. If the polymer were cross-linked, methyl groups would be replaced by Si—O—Si bridges, leading to an increase in the proportion of oxygen but a reduction in the carbon content. The composition found could result from having groups containing more than one carbon atom attached to the silicon atoms.

Table 1. Composition of composite matrix

Element, electron shell, bond type	Electron binding Energy (eV)	Approx. surface Composition (at %)
C 1s C-C, C-H	285	60.2 ± 2.6
C-O, C-N	286.7 ± 0.1	16.0 ± 2.5
O 1s	533.9 ± 0.2	4.5 ± 0.9
	532.4 ± 0.2	12.5 ± 1.9
Element, electron shell, bond type	Electron binding Energy (eV)	Approx. surface Composition (at %)
N 1s N-C	399.6 ± 0.2	399.6 ± 0.2
S 2p	168.4 ± 0.2	2.3 ± 2.0
Si 2p	102.2	0.9 ± 0.9

Table 2. Composition of release agent with Complete coverage of coating

Element, electron shell, bond type	**Electron binding Energy (eV)**	**Approx. surface Composition**
Fluorine-containing release agents		
C 1s C-C, C-H	285	2.5 ± 1.4
C-O	286.7 ± 0.1	0.4 ± 0.1
$C-F_2$	292	31.5 ± 0.9
O 1s	532.3 ± 0.7	0.7 ± 0.5
F 1s	689.1 ± 0.3	65.1 ± 1.5
Silicon-containing elastomers		
C 1s C-C, C-H	285	50.7 ± 2.9
O 1s	532.7 ± 0.2	31.2 ± 1.2
Si 2p	102.6 ± 0.1	21.0 ± 1.2
Silicone-coated glass cloths		
C 1s C-C, C-H	285	50.7 ± 2.9
C-O	287.4 ± 0.4	3.9 ± 1.5
O 1s	532.2 ± 0.1	29.2 ± 1.7
Si 2p	102.4	15.4 ± 2.5
N 1s	399.2	0.5 ± 0.6

The analyses of five coated polyamide cloths indicated that they were silicone-coated also. Coverage of four cloths (N3, N11, N20 and N21) averaged 92 + 7% silicone coverage: the fifth cloth (N12) had ~60% coverage.

One glass cloth (G5) was described by its supplier as being coated with silicone. The XPS analyses for three other coated glass cloths were similar and it was deduced that these also were silicone coated. Their composition is given in Table 2 and is very similar to that for silicone elastomers, but with reduced silicon and greater carbon content. Had there been any areas of glass exposed, increases in oxygen and silicon content would have been expected. It is assumed, therefore, that the cloths are coated with a different silicone resin to that used in the silicone elastomers and on the polyamide cloths.

Eight cloths were described by their manufacturers as being scoured heat-set polyamide, and four others were known to be polyamide, one being described as untreated. Of these, three had approximately the same composition as the scoured heat-set cloths. One release film was known to be Nylon 6, $[—NHCO(CH_2)_5—]_n$, and a second film was found to have a similar composition. Analyses are given in Table 3, from which it can be owing to inexactness of deconvolution, and was felt not to be suitable for estimation of contamination.

Table 5. Transfer of Silicone to composite surfaces and its removal by pretreatments

Release agent type	Transfer		Abraded		Grit blasted	
	Code	Transfer (%)	Code	Transfer (%)	Code	Transfer (%)
Elastomer sheet	S1 – S5	35 ± 13			S1 – S5	0
	S6	65 ± 20	S6	49 ± 8	S6	24 ± 22
Mould release agent	R1	88				
	R2	47				
	R3, 1st	1 –38, 36 - 70	R3, 1st	10	R3, 1st	1
	R3, 2nd	8	R3, 2nd	2	R3, 2nd	12
	R3, 3rd	29				
Coated polyamide release cloth	N3	60	N3	3 - 30	N3	1 - 30
	N3A	61 - 47	N3A	16	N3A	4
	N11	41 – 55				
	N20	26 – 46				
	N21	70 – 80				
Coated glass cloth	G5	76 – 80				
	N22	26 - 26	N22	7	N22	10

Table 6. Transfer of polyamide to composite surfaces and its removal by pretreatements

Release agent type	Transfer		Abraded		Grit blasted	
	Code	Transfer (%)	Code	Transfer (%)	Code	Transfer (%)

Polyamide scoured heat –set cloth	N1, N2, N2A	87 ± 18	N2A, N7	57/12	N2, N2A, N7	52/5
	N4, N5, N6, N24		N10, N14		N10, N14	
	N7, N10, N14		N24		N24	
	N15	66	N15	42/16	N15	42/0
Untreated polyamide cloth	N23	50	N23	42/14	N23	43/0

The alternative method of estimating silicone transfer was by apportioning the oxygen 532.3 eV and silicon peaks between resin and silicone. The results of this procedure are given in Table 5. Where a range is given, the two values are for the Si and O ls 532 eV peaks, respectively. Otherwise, the value is the average of the two values where these were < 10% different. As can be seen, the transfer calculated from the Si peak was often substantially less than that calculated from the O ls 532 peak, which again may be related to difficulties in deconvolution of oxygen peaks Often, substantial transfer of silicone to the composite surface took place. Only mould release agent R3, on two out of four samples, gave low transfer. It is probable that, except for elastomer 56, the layers of transferred silicone were relatively thin compared to PTFE as hand abrasion was much more effective in reducing contamination. Again, grit blasting was rather more effective than abrasion. Possible transfer from polyamide release cloths was even more difficult to estimate than from silicone-coated cloths (Table 6). Comparison of peak binding energies for resin matrix and polyamide cloths (Tables 1 and 3) show that the significant differences between the materials are the presence of the C- O peak at 288 eV, which was not found in the resin matrix, a difference of 1 eV in the position of the major component of the O ls peaks and differences in the intensity of the N ls and C—O peaks. Transfer was estimated by apportioning the N ls peak between resin and polyamide and using the C30 peak intensity. The overall average for 12 measurements on 9 cloths is given in Table 4: the two estimates for each-were usually within 20%. Transfer from cloth N15 was substantially less than from most other cloths, and that from the apparently untreated polyamide, N23, was even lower.

Estimation of residual polyamide on pretreated surfaces was less reliable: two figures are given in Table 6, the first being the estimate derived from the carbonyl group and the second that from the N ls peak. It can be seen that, while the nitrogen content of the surface was little or no greater than that of the resin, there was a large excess of carbonyl. These estimates were based on the composition of fractured bulk resin and composite. However, the composition of grit-blasted surfaces that were apparently free of the original PTFE or silicone contaminants was not the same as that of the bulk resin: in particular, there was a component of the C ls peak at 288.3 + 0.3 eV amounting to 4.0% and the N ls peak was reduced from 2.7% to 2.0%. If the residual polyamide on treated surfaces molded against polyamide cloths is estimated using these values for C=0 and N, then the surface composition of hand-abraded composites was 15% C=O/22% N and that of grit-blasted composites was 7% C O/9% N. Although the variation about these averages was ~16%, the contaminant contents were more in line with what would have been expected, i.e. that surface treatment reduced contamination. The implication from this was that the composition of the resin near the composite surface was different from the bulk. This could be due either to a genuine difference in chemical composition near the surface, owing to molecular segregation during cross- linking, or to attachment of oxygen to the surface during abrasive treatment.

OSEE analysis

Analysis was carried out on strips of composite ~50 mm wide by ~300 mm long: one-third was left untreated, one-third was hand abraded and one-third was grit blasted (three passes). A typical scan for a surface molded against' polyamide N15 is shown in Fig. 1. The average signal over an area in the centre of each treatment band was calculated. Signals tended to be low for untreated surfaces and approached the maximum of 10 for grit-blasted surfaces, with hand abraded surfaces at an intermediate level. From Fig. 2 it can be seen that, with the exception of three points, there does seem to be a regular relationship between the OSEE signal and contaminant coverage estimated from the XPS analyses.

An alternative method of relating OSEE and XPS analyses is illustrated in Fig. 3. Here, the OSEE signal is shown as a function of the nitrogen content of the surfaces: the intensity of the N ls peak was, of course, used in the estimation of polyamide transfer but not for PTFE or silicone transfer. The data at OSEE signal values of > 6 lie in a common band, but at lower signals they lie in two distinct regions, one for contamination by

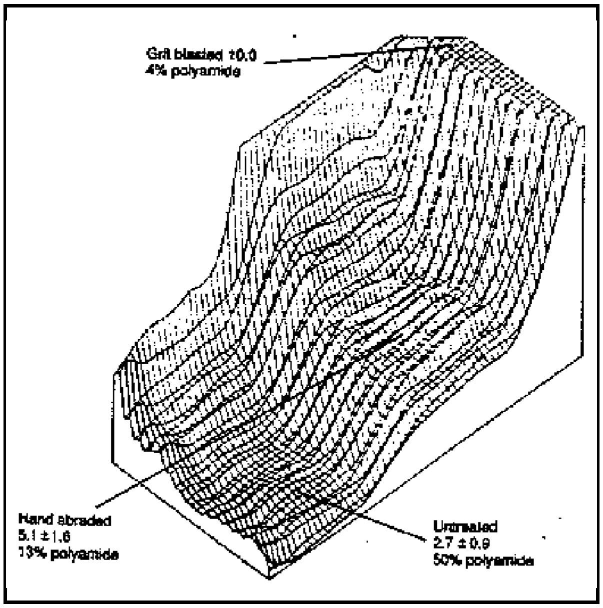

Figure 1. OSEE scan of composite surface moulded againest N15 polyamide cloth.

PTFE and silicone where the nitrogen of the matrix resin was hidden by contaminant, and a second band for polyamide contamination where the N ls peak was enhanced by the higher nitrogen content of the polyamide. From this, it was concluded that surfaces giving a signal of > 6 could be regarded as 'clean'.

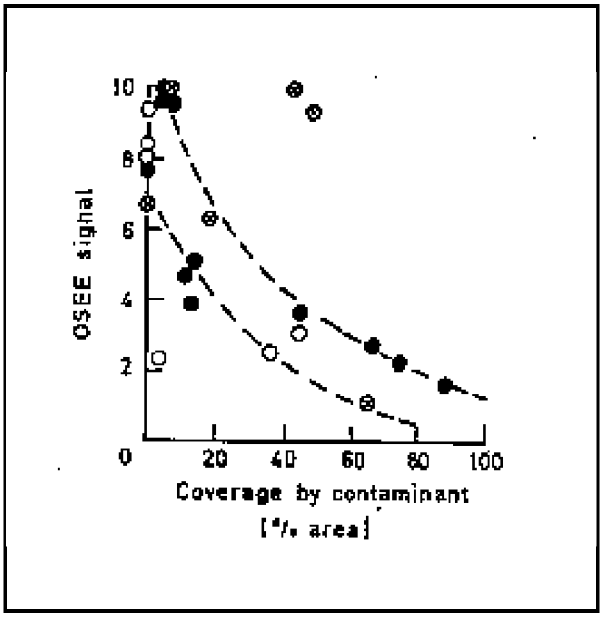

Figure 2. Relationship between composite surface contamination (estimated by XPS) and OSEE signal: (F) PTFE contamination; (-F-) silicone contamination; (M) polyamide contamination.

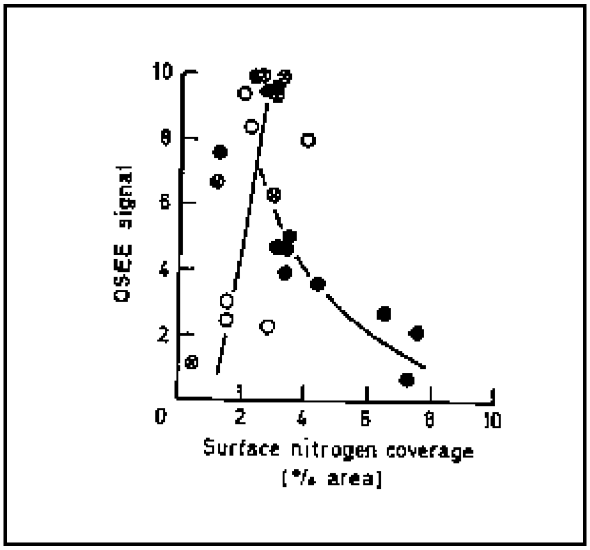

Figure 3. Relationship between surface nitrogen content by XPS and OSEE signal: (F) PTFE contamination; (-F-) silicone contamination; (M) polyamide contamination.

Adhesive-bonded joints

Single lap and peel joint strengths are plotted as functions of the OSEE signal in Figs 4 and 5, respectively. The treatment of the composite before bonding is identified by different symbols. From both figures it can be seen that, apart from one aberrant peel strength, there was a relationship between the OSEE signal and strengths measured by both types of bonded joint. There was also a very marked effect of composite surface treatment: untreated surfaces~resulted in low OSEE signals and low bond strengths, while grit-blasted surfaces gave high

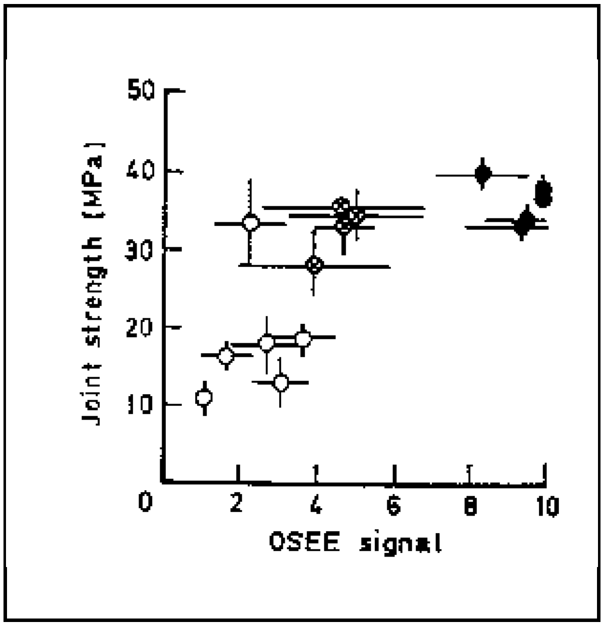

Figure 4. Relationship between strength of adhesive bonded single lap joint strength and OSEE signal: (F) untreated composite; (-F-) hand abraded; (M) grit blasted.

signals and high joint strengths. Hand-abraded surfaces gave intermediate results

The estimated percentage of interfacial failure in the lap joints is shown as a function of the OSEE signal in Fig. 6. From this, it is clear that, without grit blasting, failures were almost completely interfacial. Bands for interfacial failure, failure in the adhesive and mixed failure are shown in Fig. 5 for peel joints: only one set of joints that were not made with grit-blasted composite showed no interfacial failure.

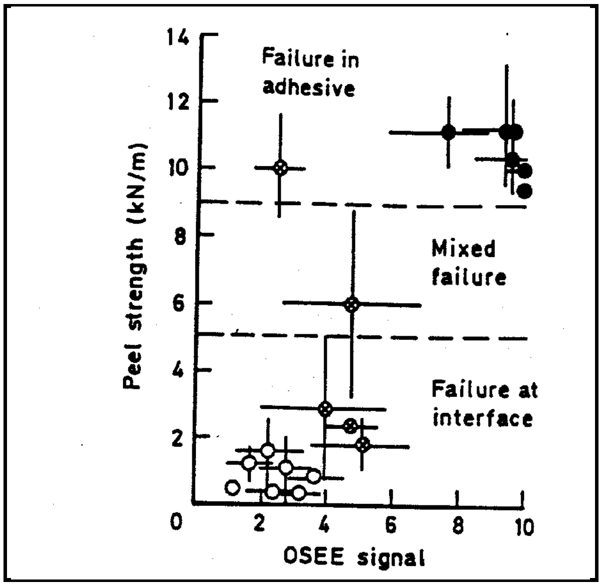

Figure 5. Peel strength of adhesive bonded joints as a function of OSEE signal: (**F**) untreated composite; (~~F~~) hand abraded; (**M**) grit blasted.

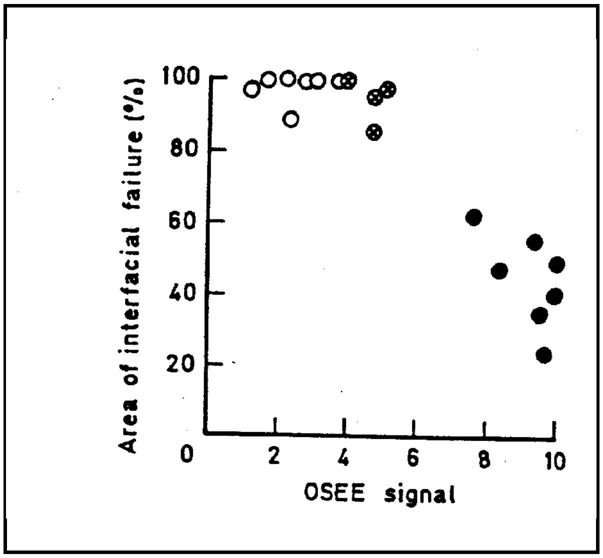

Figure 6. Mode of failure of adhesive bonded lap joints as a function of surface OSEE signal: (**F**) untreated composite; (~~F~~) hand abraded; (**M**) grit blasted.

CONCLUSIONS

XPS analysis of the surfaces of epoxy resin composites moulded against a wide range of release agents showed that, in all cases, there was some transfer of release agent onto the composite surface. This applied to both 'active' release agents, such as PTFE and silicone, and to uncoated polyamide release cloths. Comparison with the XPS analyses of the release agent themselves allowed the extent of transfer to the composite surfaces to be esimated. Abrasive treatment of the composite surface reduced the contaminant coverage, blasting with dry alumina grit being more efficient than hand treatment with abrasive cloth.

Surface were examined also by OSEE and a reasonable correlation was found between the OSEE signal and the XPS analysis when the latter was taken in the form of estimated contaminant coverage or as the nitrogen content of the surface.

There was a strong relationship between OSEE signals and adhesive bonded joint strengths, both lap joint and peel, and with the treatment of the composite surface before bonding. In order to ensure high joint strengths and low proportions of failure at the adhesive/ composite interface, an OSEE signal of ~60% of the maximum obtainable from the cleanest possible composite surface is required, a value that agrees wlth that obtained from the comparison of XPS and OSEE data. While further work is required to characterize it more fully, UV photoelectron emission does appear to be a possible method for the non-destructive quality control of surfaces of epoxy resin matrix composites before adhesive bonding.

Acknowledgement

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