

**THE USE OF DESIGN OF EXPERIMENTS TECHNIQUES TO DETERMINE THE
RELATIVE EFFECTIVENESS OF SILANE COUPLING AGENTS ON THE
DURABILITY OF TITANIUM ALLOY JOINTS. A CASE STUDY**

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ABSTRACT

This report uses design of experiments (DOE) techniques to qualify the effect of silane coupling agents on the durability of titanium joints. This study is one of a series of durability case studies that will be used to demonstrate the use of the design of experiments analysis technique to quantify the interaction of the critical factors which give rise to environmental failure. The effect on the durability of titanium alloy joints was investigated for three epoxy adhesives and five surface pretreatments; grit-blasting, two types of silane treatment, sodium hydroxide anodising and catalytic etching. The data were sourced from the paper by Stone (DERA), [1] and permission was kindly granted to reproduce some of the data presented in that paper.

The main conclusions were:

- that grit-blasting gave a low durability for all the test adhesives examined.
- the silane pretreatments were more effective than grit-blasting only.
- anodising pretreatment gave the highest resistance to crack growth

The general trend was noted for the ranking of the pretreatments in the order of highest resistance to crack growth;

Sodium hydroxide anodising >>> γ - glycidoxypropyltrimethoxy silane $\geq$ catalytic etching > γ - aminopropyltrimethoxy silane > grit-blasting.

The comparison between the traditional approach, that is the graphical comparison of a variable which changes with exposure and an analysis based on design of experiments, which removes the influence of other variables from the analysis, has confirmed that the two methods yield similar results. What makes the DOE technique so useful is that it allows the researcher to rank the effects of a parameter and parameter inter-relationship on the process being investigated.

It must be stressed that this analysis is based on data from 1988, since then the technology and understanding of surface treatments has advanced due to an active collaborative research programme. The effects of preparatory and application techniques on the relative effectiveness of silane treatments is under rigorous examination.

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1. INTRODUCTION

This is one in a series of case studies that will be used to demonstrate the use of DOE analysis technique to quantify the interaction of the critical factors which give rise to environmental failure. This report uses design of experiments (DOE) techniques to quantify the effect of a number of surface pretreatments on the environmental durability of titanium alloy joints. This analysis is based on the data of Stone (DERA) [1] obtained from Boeing wedge cleavage tests carried out at 50°C/95% relative humidity.

2. MATERIALS

The adherends were 2mm thick titanium 6Al-4V alloy, to specification BS 2TA10. The joints for the Boeing wedge cleavage test were made using three adhesives. Adhesive A was a two-part epoxy cured overnight under a vacuum blanket (65 kPa.) at $20 \pm 2^\circ\text{C}$. The joints were kept at the cure temperature for at least ten days prior to the tests being performed. Adhesive B was a supported toughened epoxide film which was cured for thirty minutes at 120°C . Adhesive C was a supported toughened epoxide cured for 60 minutes at 175°C . Joints made using adhesives B and C were compressed using a pressure of 180 kPa. in a press. One to two percent by weight glass ballotini (glass spheres) of 0.1mm diameter was added to the adhesives to control the glue line thickness.

3. PRETREATMENTS

The five surface pretreatments considered. These are as follows [1]:

- (a) *GB Grit-blasting*: This was the pre-cursor to all of the other pretreatments. The adherends were wet blasted with 180-220 grade alumina grit after degreasing using methylethylketone. The grit-blasted surfaces were then washed with tap water and then finally solvent wiped again.
- (b) *GPS - g-glycidoxypropyltrimethoxy silane (Union Carbide -A 187)*: A freshly prepared 1% solution of GPS in deionised water was left to stand for an hour or two before use. The GPS solution was brushed onto the grit-blasted adherends. The coated adherends were then positioned to drain off the excess solution and allowed to dry in air for two to three hours before use.
- (c) *APS - g-aminopropyltrimethoxy silane (Union Carbide - A1100)*: A 1% solution was prepared in deionised water and a similar procedure as applied to GPS was used to pretreat the adherends.

- (d) *SHA - Sodium hydroxide anodising*: The adherends were anodised at 10V for 30 minutes at ambient temperature in a 5M solution of sodium hydroxide using stainless steel cathodes. The titanium alloy was then washed in tap water, dried at 60°C for fifteen minutes and bonded within four hours.
- (e) *CE - Catalytic etch*: The etching solution was constituted of 1M sodium hydroxide, 0.001M manganese sulphate tetrahydrate and 0.5M hydrogen peroxide. The manganese sulphate was first added to the sodium hydroxide solution and left overnight to allow the manganese hydroxide to precipitate. The titanium adherends were then hung in the solution before the hydrogen peroxide was added. Etching was halted when the reaction stopped after approximately two to three hours. A brown discolouration was noted on the titanium. Any debris from this discolouration was wiped off and the metal was then washed and dried following the procedure for anodising.

4. TEST METHODOLOGY

The Boeing wedge cleavage test [2] was used to determine the fracture energy G . The fracture energy is used to measure the durability of the titanium/adhesive joint system, the lower the value of G , the lower the durability. One variation from the specification as laid out in ASTM D 3762 [2] was that each joint was made separately and not cut from a panel as detailed in the standard. The wedge was slowly inserted into the joints and the assembly was left overnight over silica gel before measuring the initial crack length using a travelling microscope. The joints were then exposed at the test temperature 50°C over saturated potassium sulphate solution (RH 96%) and the crack lengths were then measured at several time intervals. Fracture energies were calculated by using the relationship [1]:-

$$G = \frac{Ew^2h^3[3(a+0.6h)^2+h^2]}{16[(a+0.6h)^3+ah^2]^2}$$

where: G = fracture energy (kJm^{-2})
 E = Young's modulus of adherends
 w = displacement caused by the wedge
 h = adherend thickness
 a = crack length

Adhesive	Pretreatment	Exposure time (h)					
		0	SD	24	SD	240	SD
A	GB	1.98	±0.26	0.079	±0.044	0.067	±0.031
	GPS	2.13	±0.08	0.470	±0.029	0.232	±0.010
	APS	2.17	±0.23	0.190	±0.020	0.090	±0.017
	SHA	1.88	±0.28	0.388	±0.031	0.215	±0.018
	CE	1.90	±0.33	0.139	±0.016	0.129	±0.014
B	GB	2.37	±0.16	0.052	±0.004	0.051	±0.004
	GPS	2.48	±0.21	0.177	±0.056	0.120	±0.002
	APS	2.89	±0.41	0.098	±0.014	0.081	±0.007
	SHA	2.66	±0.35	0.982	±0.199	0.581	±0.042
	CE	2.48	±0.45	0.764	±0.447	0.414	±0.132
C	GB	0.613	±0.027	0.066	±0.001	0.066	±0.003
	GPS	0.803	±0.046	0.647	±0.013	0.397	±0.049
	APS	0.789	±0.063	0.177	±0.079	0.163	±0.061
	SHA	0.744	±0.144	0.595	±0.093	0.567	±0.113
	CE	0.734	±0.065	0.334	±0.214	0.210	±0.051

Table 1: The effect of exposure duration and pretreatment type on the mean fracture energy, G (kJ/m²) of titanium alloy/epoxide joints exposed at 50° C/96% RH.

Legend

SD = Standard deviation, three replicates

GB = grit blast only, GPS = epoxy-silane, APS = amino-silane, SHA = sodium hydroxide anodise, CE = catalytic hydrogen peroxide etch.

(Table reproduced with permission of DERA, Farnborough)

5. RESULTS AND DISCUSSION

The data used in the analysis, presented as fracture energy-time data is taken directly from Table 1 of Stone's (DERA) paper [1]. The mathematical treatment of the data follows a similar approach as discussed in a recent NPL report [3]. The data is transformed into an interaction matrix as shown in Table 1. The DOE analysis yields six 2D data-sets relating the experiment factor and its effect on durability, as measured by the reduction in the fracture energy, G, from the Boeing Wedge test.

- the effect of time. The sharp fall in fracture energy with time can be seen in Figure 1.
- the effect of the adhesive. Figure 2 gives an indication of the relative durability of the three adhesives used in this study.

- c) the effect of surface pretreatment. Figure 3 allows the comparison of the effectiveness of the surface treatments in this durability study.
- d) Figure 4 shows the interaction effect associated with adhesive and time on the durability.
- e) Figure 5 shows the interaction effect associated with adhesive and surface pretreatment on durability.
- f) Figure 6 shows the interaction effect associated with time and surface pretreatment.

In general the experimental results of Stone (DERA) [1] can be summarised as thirteen main findings. These findings are compared with the results of the analysis using the DOE method. The results of the analysis using the DOE methodology are summarised in Figures 1 to 9.

- i) **Grit-blasting gives a low durability with all adhesives.**
Figure 3 shows the main factor effect of pretreatment. This clearly shows that grit-blasting gives the lowest fracture energy. This is confirmed in Figures 5, 6 and 7.
- ii) **Both silane pretreatments are more effective than grit-blasting only.**
Figure 3 would seem to confirm this point, however, Figure 5 indicates that the effectiveness of the APS (γ -aminopropyltrimethoxy silane) treatment decreases with exposure time to close to a level similar to grit-blasting.
- iii) **GPS -(g-glycidoxypyltrimethoxy silane) is more effective than APS for all adhesives.**
Figure 3, which shows the main factor effect of pretreatment, indicates that this is true for all adhesives. This is confirmed by Figure 7 which shows a plot of the normalised fracture energy, relative to APS, against time.
- iv) **For adhesive A GPS is as effective as sodium hydroxide anodising, SHA.**
This is confirmed in Figure 6 which shows that the GPS pretreatment is as effective as SHA.
- v) **At periods up to 50 hours GPS was as effective as sodium hydroxide anodising for adhesive C.**
The graphs derived in the DOE analysis only describe the two way interactions i.e. adhesive and time or adhesive and pretreatment. This statement describes the three way interaction between adhesive, pretreatment and time. Stone (DERA) [1] describes this relationship using a graphical interpretation of the data. To obtain this relationship using DOE, this three dimensional interaction needs to be established.

The three dimensional relationship between time, adhesive and surface preparation is defined by the matrix:

A1, B1,C1	A1, B2,C1	A1, B3,C1
A1, B1,C2	A1, B2,C1	A1, B3,C2
A1, B1,C3	A1, B2,C1	A1, B3,C3
A1, B1,C4	A1, B2,C1	A1, B3,C4
A1, B1,C5	A1, B2,C1	A1, B3,C5
A2, B1,C1	A2, B2,C1	A2, B3,C1
to	to	to
A2, B1,C5	A2, B2,C5	A2, B3,C5
and	and	and
A3, B1,C1	A3, B2,C1	A3, B3,C1
to	to	to
A3, B1,C5	A3, B2,C5	A3, B3,C5

The reader can develop the 3D surface graph themselves following the techniques outlined in the previous report [3].

- vi) **Sodium hydroxide anodising gave the highest resistance to crack growth.**
Figure 5 indicates that the SHA treatment had the highest fracture energy after 240 hours of exposure, thus confirming Stone's (DERA), findings [1].
- vii) **For adhesive A there is little difference between the GPS and SHA treatments.**
The difference in fracture energies between these treatments as shown in Figure 6 is 12%.
- viii) **Adhesive A and catalytic etching, (CE) treatment is marginally better than grit-blasting.**
Figure 6 shows that the fracture energies for these two pretreatments are similar.
- ix) **Adhesive B and CE treatment approaches the durability of sodium hydroxide anodising pretreatment, SHA.**
Catalytic etch pretreatment has a fracture energy 8% less than sodium hydroxide anodising
- x) **Adhesive C and catalytic etching pretreatment, CE treatment is the middle ranking surface treatment.**
Figure 6 shows that the CE treatment has the third highest fracture energy for adhesive C, fractionally higher than the APS treatment.

- xi) **In general the GPS surface pretreatment was better than APS pretreatment.**
For adhesives A and C the GPS treatment gave higher fracture energies than the APS pretreatment. For adhesive B the APS treatment “outperformed” the GPS pretreatment by 10% from the data shown in Figure 6. However, Figures 5 and 7 indicate that over time, the GPS pretreatment gave higher fracture energies than the APS system.
- xii) **The GPS pretreatment performs almost as well as anodising, SHA..**
Figure 7 indicates that the fracture energy levels associated with the two pretreatments differ by approximately 10%.
- xiii) **Adhesive C was the least tough initially but had the highest durability whereas Adhesive A had the lowest durability.**
Figure 4 which shows the interaction between the adhesive and time confirms this conclusion.

Stone (DERA), [1] also investigated the effect of the adhesive and the pretreatment on the time taken for the fracture energy to reach 0.5 kJm^{-2} (Table 2). Figures 8 and 9 show the fracture energy values calculated in this study ignoring the effect of the adhesive. These data are tabulated in Table 3 to compare with Stone’s (DERA), [1] original figures.

Adhesive	Pretreatment	Exposure Time $G = 0.5 \text{ kJm}^{-2}$ [1]
A	GB	~0.5
	GPS	13
	APS	2
	SHA	4
	CE	~0.5
B	GB	~0.2
	GPS	7
	APS	4
	SHA	~500
	CE	140
C	GB	~0.1
	GPS	100
	APS	6
	SHA	>>400
	CE	8

Table 2 Effect of adhesive and pretreatment on exposure time for G to reach 0.5 kJm^{-2} in titanium alloy-epoxide joints exposed at $50^\circ \text{C}/96\% \text{RH}$, data taken from Stone (DERA), [1].

Pretreatment	Exposure Time $G = 0.5 \text{ kJm}^{-2}$ (hours)
GB	3.75
GPS	8.75
APS	5.5
SHA	150
CE	8

Table 3 Effect of adhesive and pretreatment on exposure time for G to reach 0.5 kJm^{-2} in titanium alloy-epoxide joints exposed at $50^\circ \text{C}/96\% \text{RH}$, DOE Analysis.

It can be seen from a comparison of the data presented in Tables 2 and 3 that the two analysis methods rank the pretreatments in a similar order as shown below.

Sodium hydroxide anodising >>> g - glycidoxypopyltrimethoxy silane ³ catalytic etching >-g - aminopropyltrimethoxy silane > grit-blasting

6. UNCERTAINTIES IN ANALYSIS

The accuracy of this study is limited due to the reduced amount of data. There was only access to three samples per condition from the published work of Stone (DERA), [1]. These data were the average values of three replicate wedge tests. For a 95% confidence level, the standard deviation of the data must be multiplied by a factor of approximately four. This factor is obtained from Students T-test statistical tables. Application of this basic statistical test indicates that the error band associated with each data point is large. In a number of cases the uncertainty associated with each data point is greater than the actual average value. This produces error bars on the compared data i.e. grit-blasting vs. silane treatment that overlap, thus reducing the validity of any assumptions drawn from the data plots. These data errors could be reduced by carrying out a greater number of replicate tests etc. The increased confidence in the data on reducing any associated experimental error would lead to a greater reliability in associating differences in durability performance with a change in surface treatment.

7. CONCLUSIONS

The comparison between the traditional method and an analysis based on design of experiments has confirmed that the two methods yield similar results. However, for some comparisons, drawing conclusions from a 2 dimensional output may lead to erroneous interpretation of the cause of the effect. This is where the DOE technique has its merits, for it allows the researcher to quantify the effects of a parameter and parameter inter-relationship on the process under investigation. This process was not carried out as the sparseness and the variation in the original input data would make definitive conclusions meaningless. However, based on the average of the input data a good pseudo-quantitative assessment of the two dimensional relationships occurring within designated experimental system can be made and qualitative assessments can be easily realised. For this study a qualitative ranking of the surface pretreatments was made. It was found that the effectiveness of the pretreatment was in the order shown below.

**Sodium hydroxide anodising >>> g - glycidoxypropyltrimethoxy silane > catalytic etching >-
g - aminopropyltrimethoxy silane > grit-blasting**

It must be stressed that this analysis is based on data from 1988, the technology and understanding of surface treatments has since advanced due to an active collaborative research programme. The effects of preparatory and application techniques on the relative effectiveness of silane treatments is under rigorous examination.

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ACKNOWLEDGEMENTS

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Figure 1: The Effect of Time on the fracture energy

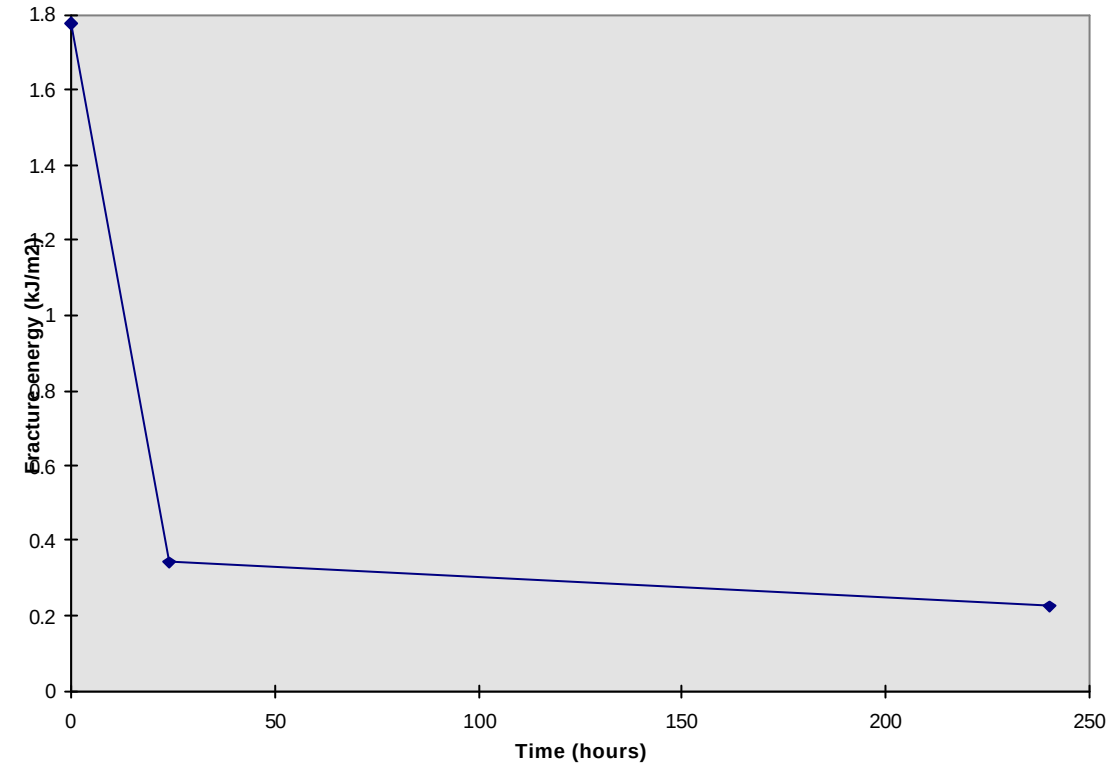


Figure 2: The Effect of the Adhesive on the fracture energy

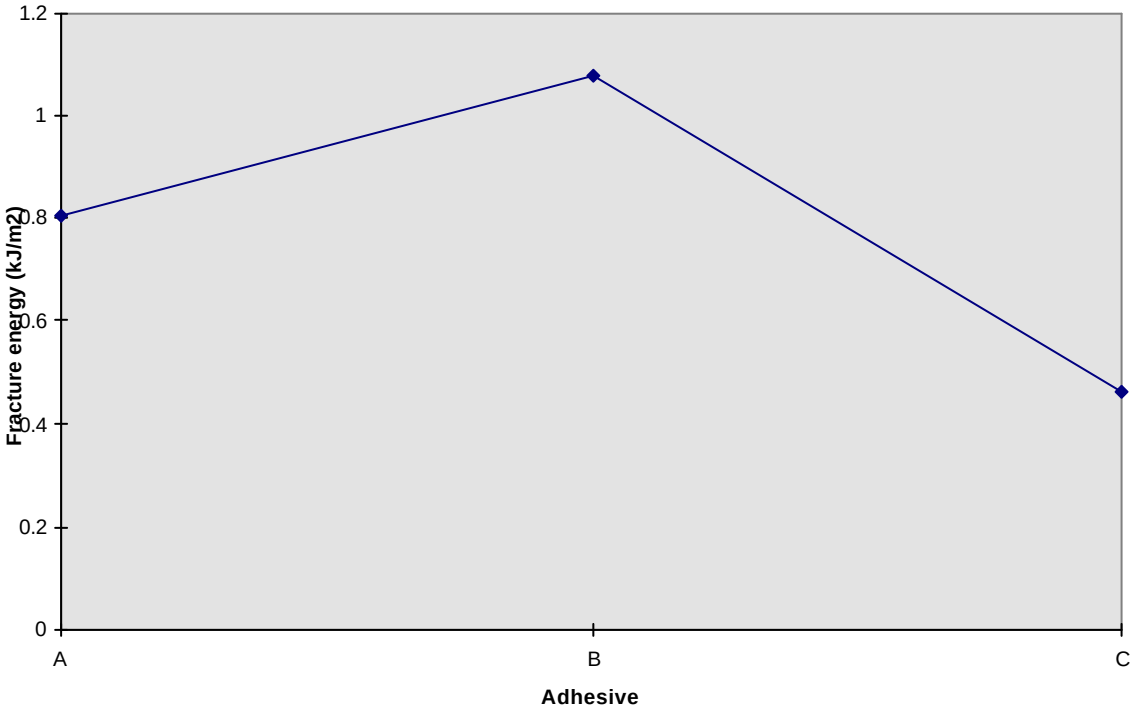


Figure 3: The Effect of Pretreatment on the fracture energy

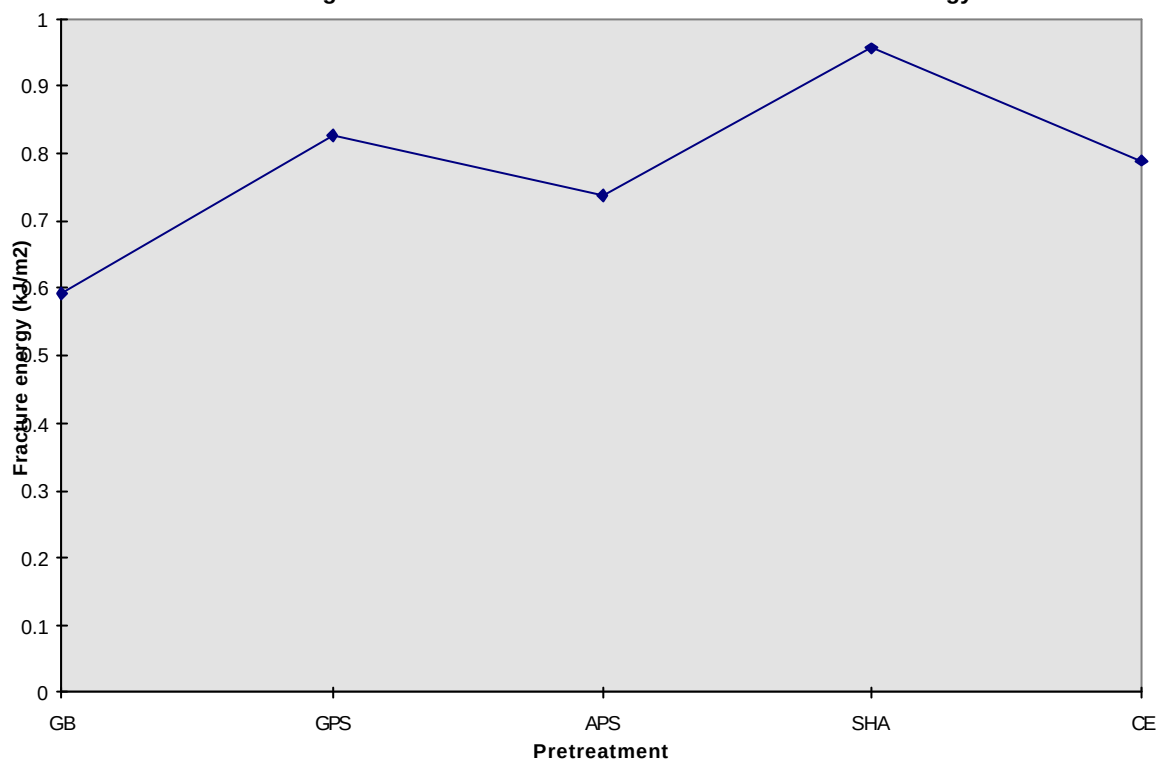


Figure 4: The Effect of the Interaction between Adhesive and Time on fracture energy

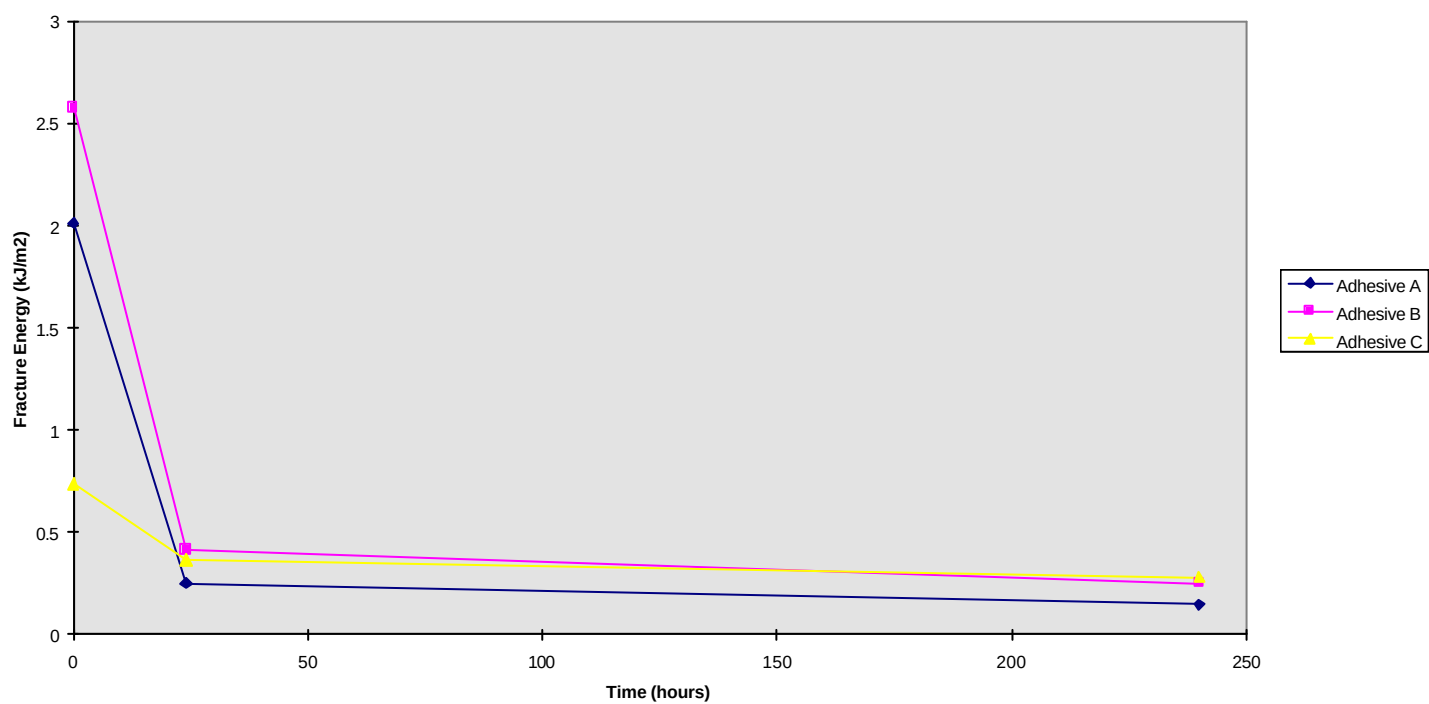


Figure 5: The effect of the Interaction between Time and Pretreatment on the fracture energy

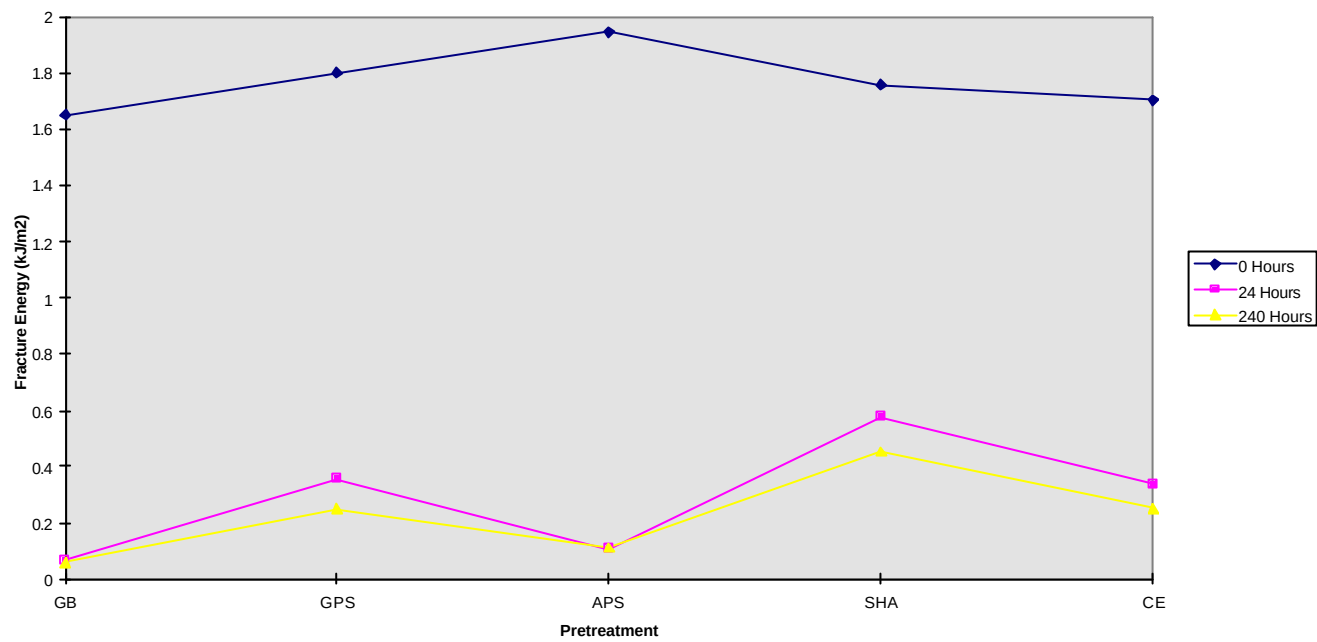


Figure 6: The effect of the Interaction between Adhesive and Pretreatment on the fracture energy

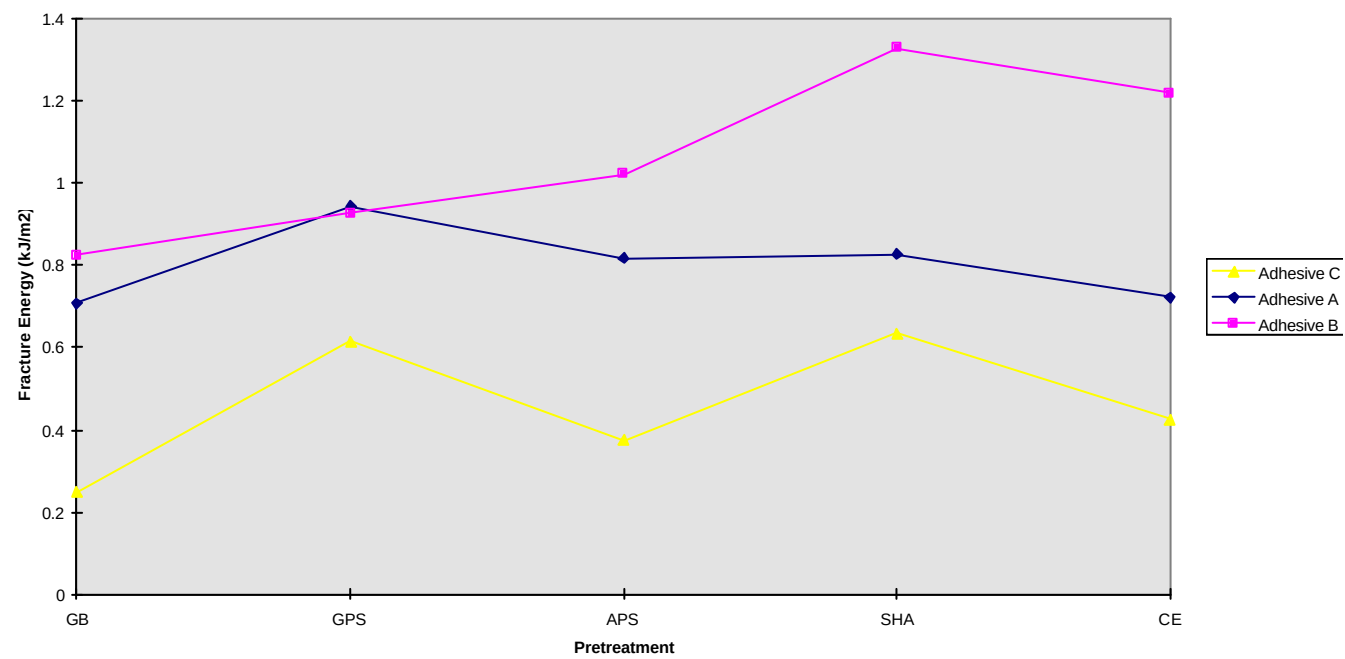


Figure 7: Durability of Pretreatment independent of Adhesive (normalised relative to APS pretreatment)

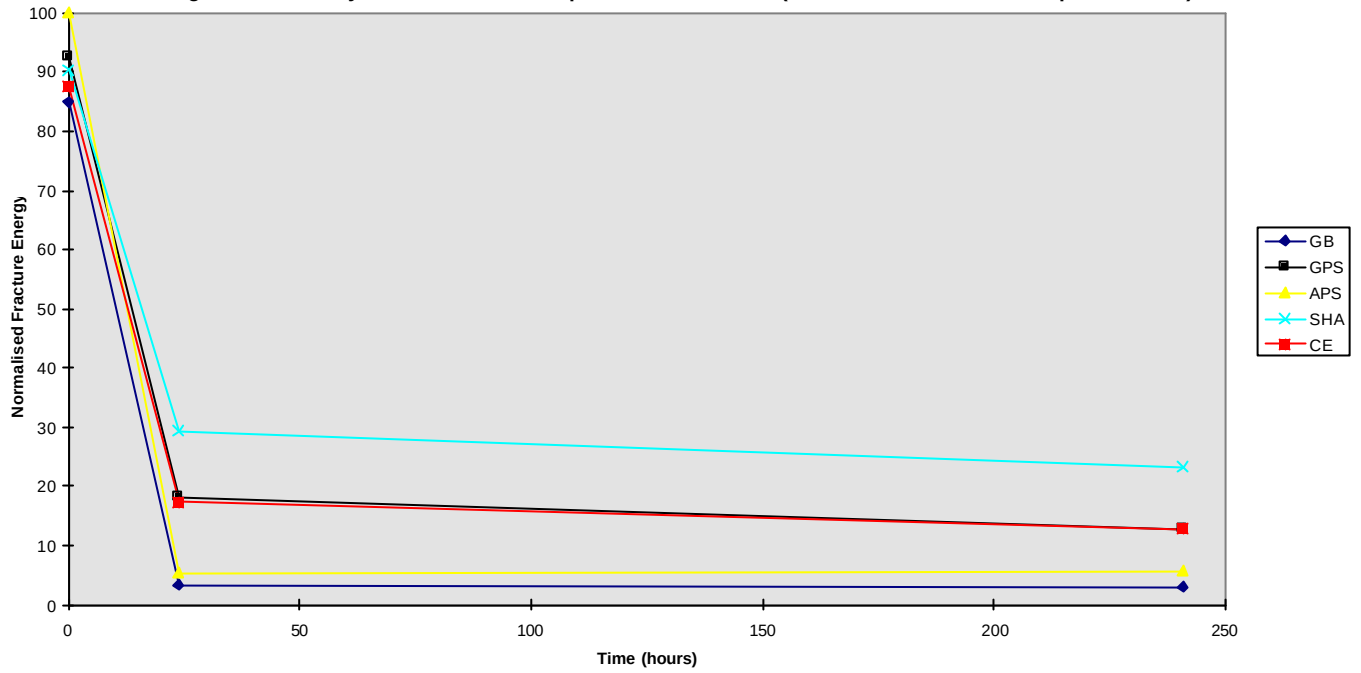


Figure 8: The Effect of pretreatment on exposure time for the fracture energy to reach 0.5 kJ/m² at 50C/96%RH

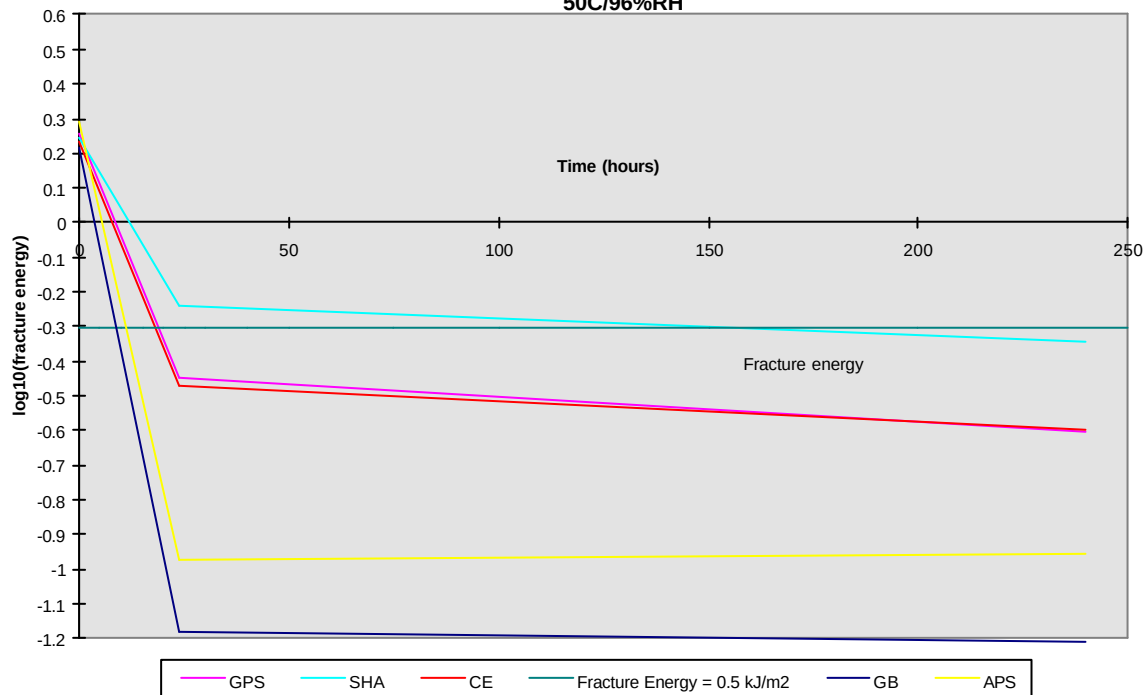


Figure 9: The Effect of pretreatment on exposure time for the fracture energy to reach 0.5 kJ/m2 at 50C/96%RH

