



Reilly, S.P. and Thomason, J.L. (2010) Effects of silane coating on the properties of glass fibre and glass fibre reinforced epoxy resin. In: 14th European Conference on Composite Materials, ECCM14, 7-10 June 2010, Budapest, Hungary.

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## EFFECTS OF SILANE COATING ON THE PROPERTIES OF GLASS FIBRE AND GLASS FIBRE REINFORCED EPOXY RESIN

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### Abstract

*Single fibre tensile testing and microbond testing have been used to benchmark the influence of silane coupling agents on the performance of glass fibre for reinforced epoxy resin composites. Retention of fibre strength and optimisation of the fibre-matrix interphase in such composites is critical for improving performance for the longer term reliability of that performance. This poster will focus on a key component in the formation of that interphase, the fibre surface sizing and in particular on the critical role of the silane used in these sizings. It is thought that these coupling agents can directly control the stress transfer capability of the interphase and also play a defining role in the long term performance of composites-through their influence on adhesion and fibre strength.*

*Glass fibre samples were coated with single and blended silanes and these fibres were characterised by single fibre testing for strength and modulus. The effect on interfacial strength in epoxy resin has been measured using the microbond test. The results of the single fibre tensile testing demonstrated that the fibre strength improves with single silane application and that applying a blend of silanes has a synergistic result. The adhesion results from the microbond tests will also be discussed.*

### 1 Introduction

The goal of this project is to benchmark the performance of silane coupling agents on the critical performance parameters of glass fibre reinforced epoxy resin composites. This project will focus on the key component in the formation of that interphase; the surface coating (or sizing) and in particular on the critical role of the silane coupling agents used in these sizings.

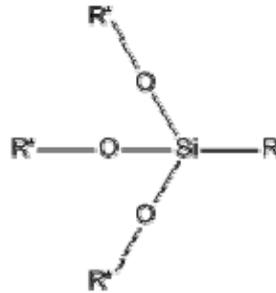
This project builds upon work carried out in a research project [1] studying the interactions of silanes with the surface of glass fibres. One of the main results of that work was that the structure of the silane interphase on glass fibres formed from blends of silanes can be tailored by the choice of the ratio of silanes in such a blend. In this project glass fibre samples will be coated with single and blended silanes. The influence of these coatings on the fibre strength and fibre-matrix adhesion will then be discussed.

#### 1.1 Literature Review

It is widely accepted that the level of adhesion between fibre and matrix affects the ultimate mechanical properties of a composite. However less researched is how the mechanical properties of the fibre also affect the composite as a whole. To tailor the interface between the fibre and matrix and to alter the mechanical attributes of the fibre, a sizing is added to glass fibres after production. This sizing also protects the fibre during handling and increases the wettability of the fibre surface by the molten polymer or reactive mixture of



monomers[2]. The sizing is a mixture of lubricant, antistat, binder and coupling agent and here 5 silanes are investigated as coupling agents. The five silanes are trialkoxy silanes of the general form shown in figure 1.



**Figure 1** Trialkoxy silane general form

Where R is a polymer-compatible or polymer-reactable organic group and R' is either ethyl or methyl[3]. The silanes can react at the glass surface with hydrolysed silanol groups and favour the chemical coupling with the sizing as well as with the surrounding matrix in order to promote the interfacial adhesion[2]. Fibre strength is often described as following the weakest-link theory which assumes that the material will fail at the most detrimental flaw. Size effects occur due to the decreased possibility of a smaller volume containing severe flaws. [4]Composite strength in the fibre direction is directly influenced by the fibre strength.

As determined in previous work [4]60 tests were required for a reliable Weibull analysis of the fibre strength results and to ensure 60 good results were achieved, 90 tensile test samples of each silane were created.

Single fibre tensile testing is a simple, direct method for measuring individual fibre strength. The common tests for determining the adhesion properties of the fibre to the matrix are however much less simple. These tests generally fall into two categories, Micro-mechanical or Macro-mechanical. The most common micromechanical tests are microbond, single-fibre pull-out, fragmentation and micro-indentation tests. For studying the interphase at a macro-mechanical level the methods used include tensile test, Iosipescu and short beam shear. Here we will be using the microbond test to quantify the affect of the different silanes on the fibre-resin interphase.

In the microbond test a droplet of resin is deposited on the fibre surface and cured. This fibre is then mounted in a test rig, and the droplet is sheered off the fibre using a custom-built microvise. The interfacial shear strength is then calculated by dividing the maximum measured force at debonding by the surface area of the fibre which is embedded inside the droplet[5]. This result will not however be a true measure of adhesion and it is widely debated wither any of the micro-mechanical tests do in fact provide this measurement. In the microbond test the state of stress can vary with both the size of the droplet and how it is exactly positioned against the microvise blades[5], however it is a sensitive test that can be used to measure any fibre and resin combination. It will be used here to compare the effectiveness of the silanes and silane blends to improve the fibre strength and the fibre-matrix interphase.



## 2 Experimental

### 2.1 Materials

The fibre used was E-glass fibre from Owens Corning and the silanes used and their designations are given in the following table:

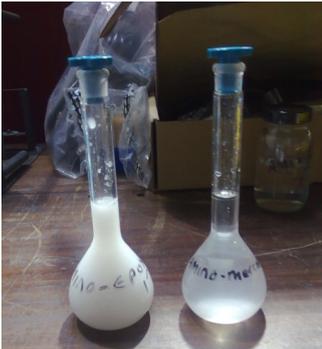
Designation	Sizing	Chemical Structure	Ave fibre Ø (µm)
VS	Vinyltriethoxy Silane	$\begin{array}{c} \text{OCH}_3 \\   \\ \text{H}_2\text{C}=\text{CH}-\text{Si}-\text{OCH}_3 \\   \\ \text{OCH}_3 \end{array}$	17.27
Methacryloxy-PS	γ-methacryloxypropyltrimethoxy Silane	$\begin{array}{c} \text{O} \\    \\ \text{H}_2\text{C}=\text{C}-\text{COCH}_2\text{CH}_2\text{CH}_2-\text{Si}-\text{OCH}_3 \\   \qquad \qquad \qquad   \\ \text{CH}_3 \qquad \qquad \qquad \text{OCH}_3 \end{array}$	17.58
GPS	γ-Glycidoxypropyltrimethoxy Silane	$\begin{array}{c} \text{H} \\   \\ \text{CH}_2-\text{C}-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-\text{Si}-\text{OCH}_3 \\ \diagdown \quad   \\ \text{O} \qquad \qquad \qquad   \\ \qquad \qquad \qquad \text{OCH}_3 \end{array}$	18.6
MPS	γ-mercaptopropyltrimethoxysilane	$\begin{array}{c} \text{OCH}_3 \\   \\ \text{SH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-\text{OCH}_3 \\   \\ \text{OCH}_3 \end{array}$	18.44
APS	γ-Aminopropyltriethoxysilane	$\begin{array}{c} \text{OCH}_2\text{CH}_3 \\   \\ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-\text{OCH}_2\text{CH}_3 \\   \\ \text{OCH}_2\text{CH}_3 \end{array}$	17.96
Owens APS	γ-Aminopropyltriethoxysilane	$\begin{array}{c} \text{OCH}_2\text{CH}_3 \\   \\ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-\text{OCH}_2\text{CH}_3 \\   \\ \text{OCH}_2\text{CH}_3 \end{array}$	16.78
Owens Unsized	Owens water	H <sub>2</sub> O	18.03
Water Sized	Water	H <sub>2</sub> O	18.69
PH Normal APS	APS	APS	18.22
APS+MPS	APS+MPS	APS+MPS	17.09
APS+GPS 50/50	APS+GPS	APS+GPS 50/50	17.63
APS+GPS 90/10	APS+GPS	APS+GPS 90/10	17.69

**Table 1** Silanes and their chemical structures



## 2.2 Silane treatments

The hydrolysing of silane in water is aided by adjusting the pH of the deionised water to 5-5.5, using a diluted acetic acid solution. The pH was measured using a pH meter which was calibrated using pH 4, 7 and 10 buffer solutions. A 1% solution of each silane was created. As amino silanes (APS) don't require an acidic solution to aid solubility in water, a fibre bundle was also sized with APS solution at pH7. Each solution was left for 24 hours. Four blended silane solutions were also produced. Three of these were created from 1:1 mixtures of two silanes, each at 1% concentration and the fourth at 9:1 ratio.



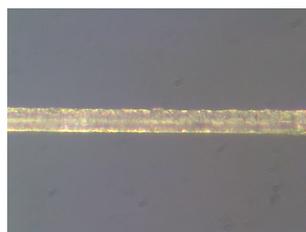
**Figure 3** Turbid solutions



**Figure 2** Aggregates in silane solution

The uncoated glass bundles were completely immersed in the silane solutions for 15 minutes at room temperature. A series of papers produced by Yue and Quek[6] has determined that the immersion time does not affect the amount of silane on the dried fibres; this is determined by the concentration of the solution. Each bundle was dried in an oven at 110°C for 15 minutes. It was observed that during the 24 hours that the solutions were left to hydrolyse, some developed a turbid appearance (figure 3). In other cases aggregates were formed in the solution (figure 4). This resulted in the fibres being coated with a white layer which flaked off when the fibres were later separated during sample preparation. This layer could be seen under the microscope (figure 5).

Further investigation of the literature has revealed that most methods of hydrolysing silanes for coating fibres include a final rinsing stage where excess solution is washed off to avoid particle growth affecting the testing. Yue and Quek[6] investigate the effect of these agglomerates of silane with the conclusion that they do not influence the fibre-matrix adhesion. This is contradicted by Heitz et al. [7] who have studied the formation of oligomers from which the particle growth results in APS, GPS and blends of the two at different concentrations. They found that as expected Amino silanes in solution at natural pH reaches equilibrium very quickly and only extremely small aggregates form. Epoxy silane on its own



**Figure 4** Fibre with aggregates on surface



condensed initially very slowly however after 80 minutes large aggregates form. A mixture of both silanes speeds up this process. In one case an epoxy/amino silane mix at 1/0.3 wt%/wt% was coated on glass fibres at different time intervals; these were then tested for tensile strength. It was found that the fibres that had been coated after 35 minutes suffered a large drop in strength. This suggests that the silane solution degrades with age and further work should be carried out to investigate these effects.

### 2.3 Single fibre tensile testing

ASTM standard D2343-08 was followed for testing. Each fibre was then tested using an Instron Tensile Testing rig (figure 6). A 10 N load cell was used for this application as the samples tend to break between 0.1 and 1 Newton[4]. The testing machine is controlled using Bluehill testing software which allows the user to specify certain inputs and a wide range of outputs from the test. The ramp rate used for the test was calculated as 1.5% strain/min which for a gauge length of 20mm results in 0.3mm/min.

### 2.4 Microbond Test

The resin and hardener used were Araldite 506 (Sigma-Aldrich) and Triethylenetetramine hardener (Sigma-Aldrich) mixed to a ratio of 176:24. After mixing the resin it was de-gassed for 5 minutes to release any trapped air induced during mixing. Two droplets of resin were applied to each fibre a designated length from where the fibre is secured to the card. These drops were applied using a length of 150 $\mu$ m diameter steel wire. The samples were then cured for 1 hour at 120°C.



Figure 5 Instron testing rig

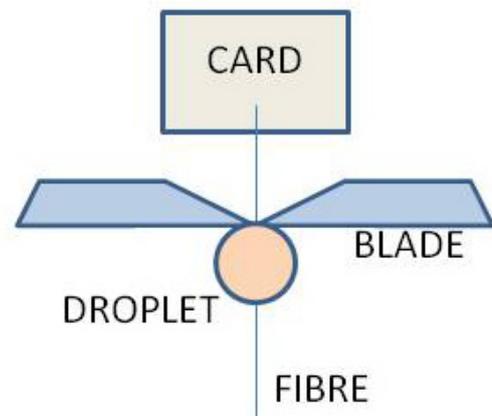


Figure7 Schematic illustration of microbond test

The microbond test was then conducted using the set up shown in figure 7. The droplet was brought to just below the microvise blade and the microvise was closed until just touching the fibre. The blades had to be consistently the same distance apart so that the stress pattern would remain the same for each test. During the test the force is applied through the card and the blades shear the droplet from the fibre. The shear strength ( $\tau$ ) required from this is



calculated by equation 1 where  $D$  is fibre diameter,  $F_{\max}$  is max force and  $L_e$  is embedded length.

$$\tau = \frac{F_{\max}}{\pi D L_e} \quad (1)$$

### 3. Experimental Results

The experimental stress strain curve was linear as expected for a brittle material. The results of the average fibre modulus and strength can be seen in figure 8. It is clear there is no correlation between and increase in strength and an increase in modulus.

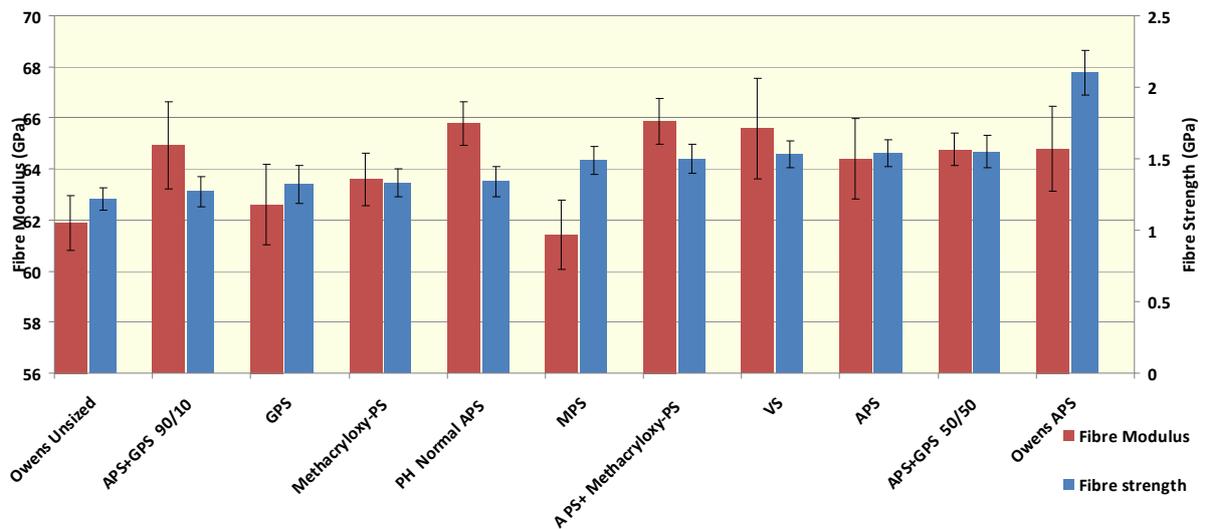


Figure 8 Average fibre modulus and strength-ranked by increasing strength

The results show that coating the fibres with any silane increases the strength and modulus of the fibre from the uncoated fibre. The increase in fibre strength is particularly large for some of the silane mixes and APS. Two of the blended silanes are blends of APS and GPS at different ratios, 50:50 and 90:10. When looking at the strength results of these coated fibres, the difference is large which suggests that the ratio within the blended silanes is a critical factor and modifying this could allow the interphase to be tailored further. The strength of the water coated fibre was compared to the original uncoated fibre and was seen to be unchanged; this shows that the handling encountered during the coating process does not result in reduced strength of the fibres. From the results it can be seen that the strength of the commercially coated APS fibres was not recreated with the silanes in the lab however APS was the most effective single silane at improving fibre strength.

The Owens APS sized fibre was the worst performer in the microbond test. These fibres have not only APS on them but also other chemicals to improve the performance of the final composite. It is possible that these chemicals reduce the interfacial shear strength while improving some other critical factor. APS and the blend APS+GPS 50/50 are also the two samples with the highest interfacial shear strength. This is to be expected as the reactivity's of APS and GPS are known match well with epoxy where as Methacryloyl-PS bonds better with polyester.

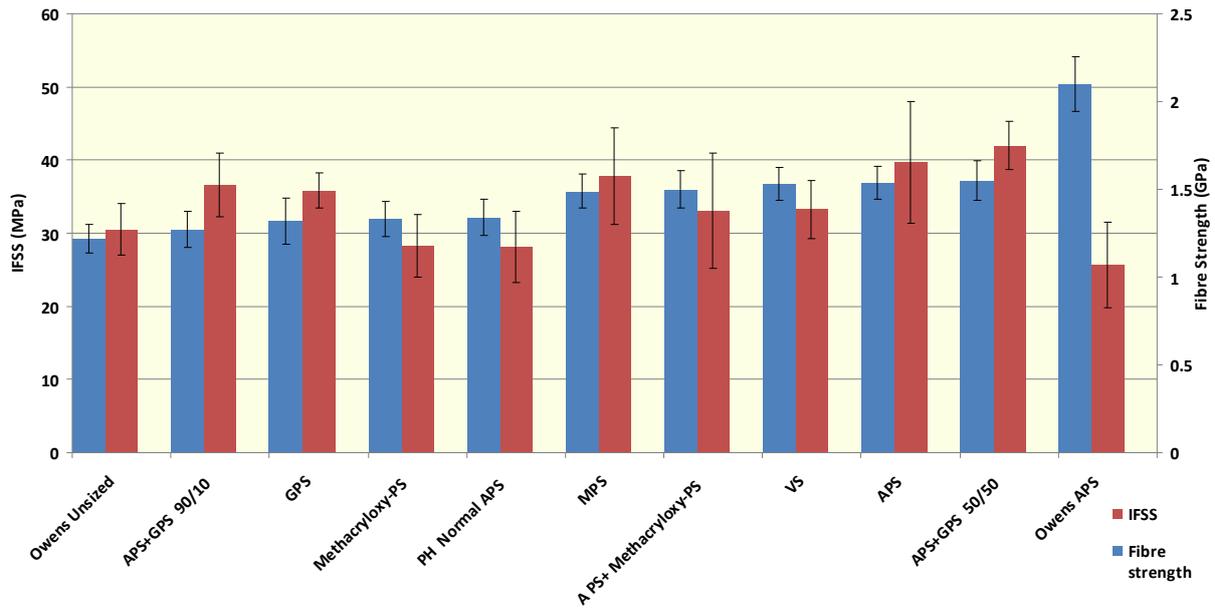


Figure 9 Average IFSS and strength-ranked by increasing strength

#### 4. Discussion

From the Weibull plots in figures 10 and 11 we can see that there are differences in the gradients of the results. The APS sized fibres and the Owens sized fibres display a unimodal distribution which has been attributed to a reduction of flaw severity due to the healing surface flaws by the deposited sizing particles[2]. The results where two distinct gradients can be identified in the line are said to have a bimodal distribution. This bimodal distribution is indicative of two different flaw types. This has been further upheld by work carried out by

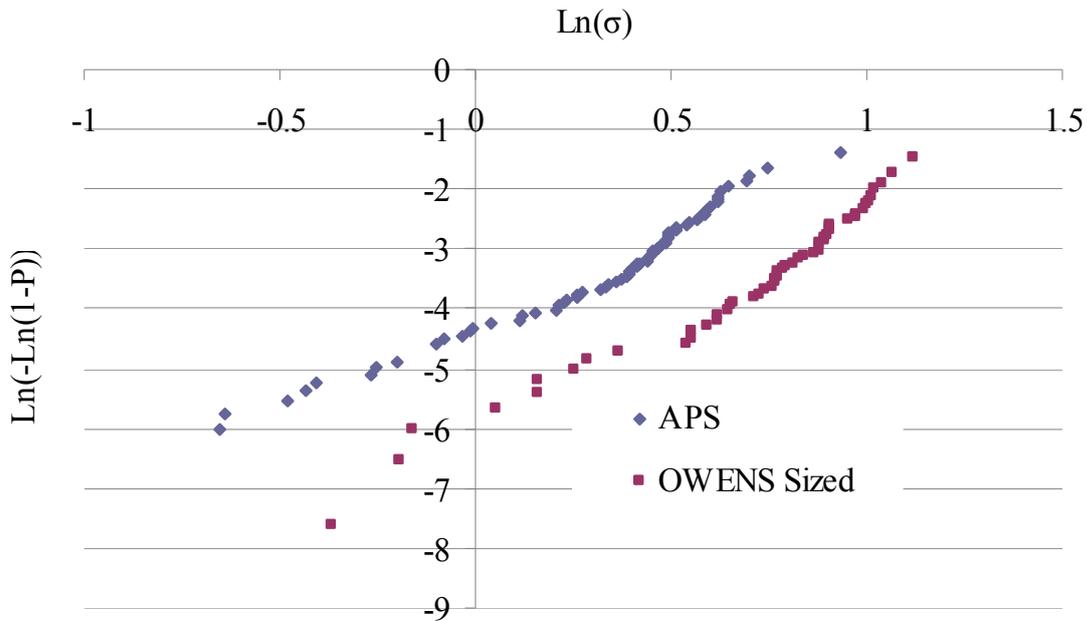
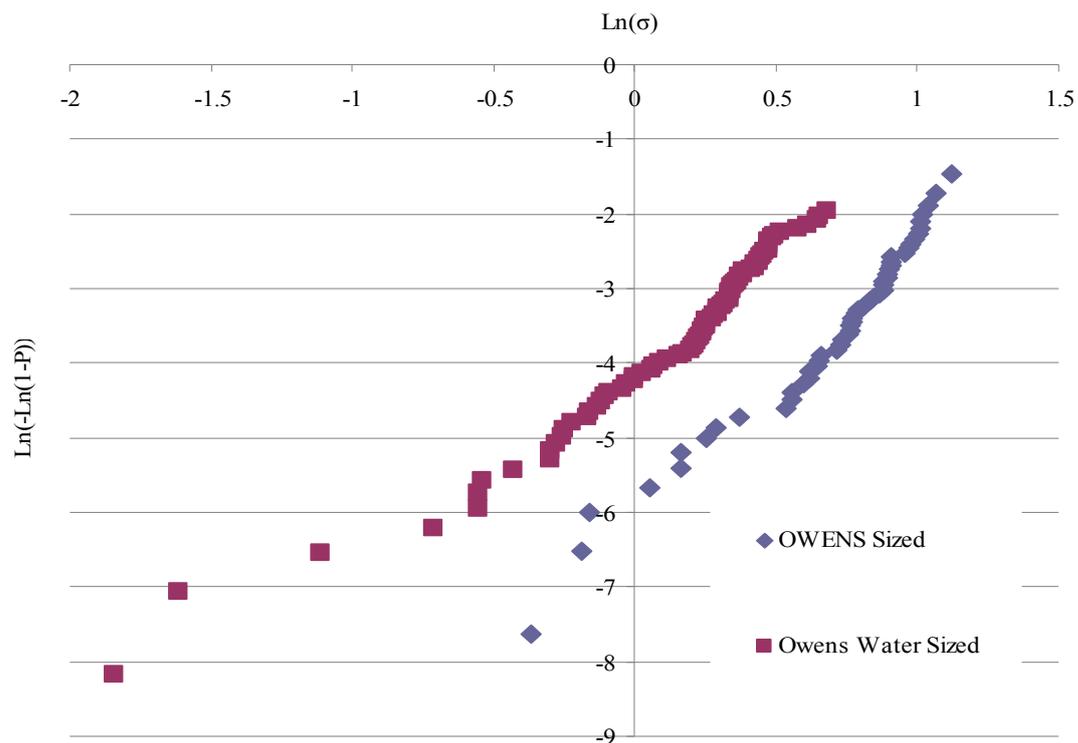


Figure 10 Weibull distribution: APS and Owens sized



Feih et al.[4] who characterised high and low strength fibre failures using a scanning electron microscope (SEM). For low strength fibres an initial small surface flaw propagated a crack, creating fracture features known as the mirror, mist and hackle. For the high strength region either a two plane failure pattern or smooth failure pattern was observed. It was reported by Schmitz and Metcalfe [8, 9] that the failure of glass fibres is governed by several flaws with varying gauge length. 3 types of failure have been highlighted for gauge length between 0.5-500mm. The third of these flaws only is apparent at a gauge length of less than 1mm. This has been further backed up by Rosen [10].

A Weibull plot of the Owens sized and unsized fibres are presented in Figure 11. As it has been noted in the past [4] both the sized and unsized fibres have similar high strength values but as the strength decreases the difference between the values becomes greater. Feih et al. also identified a threshold above which it is proposed that the silane doesn't affect the strength of the fibre. The silane is able to 'heal', to some extent, the fibres which would fail at a lower strength. Figure 12 compares the Weibull distribution of the OU (unsized) fibre and the APS+GPS 50/50 fibre which has demonstrated the highest strength. We can see that the distribution of low strength fibres has improved which correlates with the findings of Feih et al. however the high strength fibres also seem to improve in strength, suggesting that the sizing is also working in a function other than 'healing' the fibres.



**Figure 11** Weibull distribution: Owens water sized and Owens sized

The bonding between the fibre and the matrix is widely discussed, as is the affect that the silanes have on this bond. It is suggested that the ogilomers of silane on the surface fibre



could have a bad influence on the adhesion [7]. The results presented here do not agree with this. The APS+GPS blend which was mixed with two different concentrations gives us one solution, APS+GPS 50/50, where visible aggregates formed and the other, APS+GPS 90/10 where no aggregates formed after 24 hours. As APS+GPS 50/50 solution preformed better in modulus, strength and IFSS tests we can say that the particles did not affect the interface negatively.

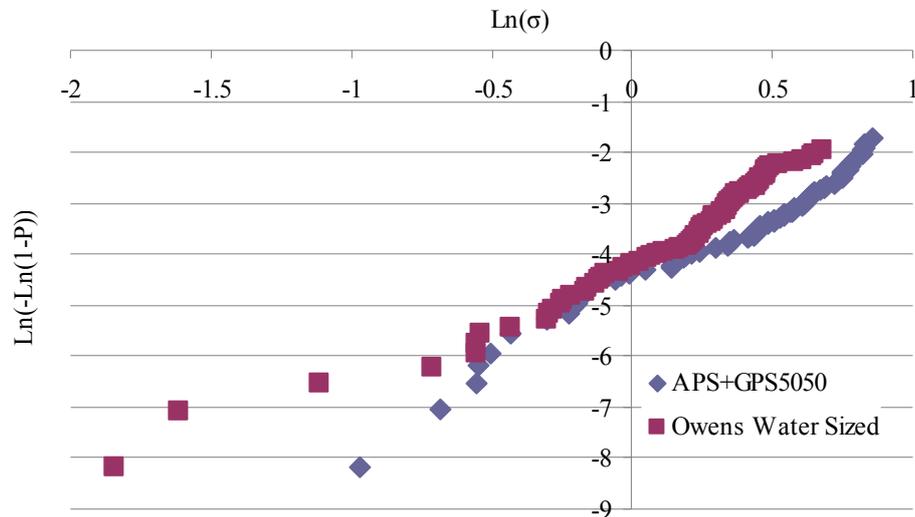


Figure 12 Weibull distribution: Owens water sized and APS+GPS50/50

## 5. Conclusion

Silane improves the strength of the fibres and this could be through 'healing' of the surface flaws. IFSS is also improved by certain silanes and by certain blends of silane. Increase in strength and in IFSS is not synonymous and we have determined that APS and the blended APS+GPS 50/50 are two coatings which perform well in both tests. It would be advantageous to study further the results of different concentrations of silanes in the blend and wither altering the age of the solution would allow an increase in fibre strength and IFSS.



### Bibliography

- [1] Liu, X.M., J.L. Thomason, and F.R. Jones, *Differentiation of silane adsorption onto model E-glass surfaces from mixed solutions of amino and glycidyl silanes*, in *Silanes and Other Coupling Agents*, K.L. Mittal, Editor. 2007.
- [2] Zinck, P., E. Mader, and J.F. Gerard, *Role of silane coupling agent and polymeric film former for tailoring glass fiber sizings from tensile strength measurements*. *Journal of Material Science*. **36**: p. 5254-5252, 2001.
- [3] Plueddemann, E.P., *Silane Coupling Agents*. New York: Plenum Press, 1982.
- [4] Feih S, A.T., H Lilholt, *Tensile strength and fracture surface characterisation of sized and unsized glass fibres*. *Journal of materials science*. **40** 2005
- [5] Herrera-Franco, P.J. and L.T. Drzal, *Comparison of methods for the measurement of fibre/matrix adhesion in composites*. *Composites*, 1992. **23**(1): p. 2-27.
- [6] Yue, C.Y. and M.Y. Quek, *The interfacial properties of fibrous composites*. *Journal of Materials Science*, **29**(9): p. 2487-2490.1994.
- [7] Heitz, C., et al., *Cross-condensation and particle growth in aqueous silane mixtures at low concentration*. *Journal of Colloid and Interface Science*, **298**(1): p. 192-201 2006.
- [8] Metcalfe, A.G. and G.K. Schmitz, *Effect of Length on the Strength of Glass Fibers*. *Proceedings of the American Society for Testing and Materials*, **64**: p. 1075. 1964.
- [9] Schmitz, G.K. and A.G. Metcalfe, *Testing of Fibres*. *Material research and Standards*, **7**(4): p. 146-152. 1967.
- [10] Rosen, B.W., *Fibre Composite Materials*. Metala Pack, Ohio: ASM. Chap. 3. 1965.
- [11] Zinck, P., et al., *Mechanical characterisation of glass fibres as an indirect analysis of the effect of surface treatment*. *Journal of materials science*. **34**: p. 2121-2133. 1999.