AN INVESTIGATION OF FIBRE SIZING ON THE INTERFACIAL STRENGTH OF GLASS-FIBRE EPOXY COMPOSITES

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Abstract
The fibre surface coating (or sizing) is one of, if not *the*, most crucial components involved in the manufacture of glass-fibres and plays a key role in determining the profitability, processability and both long- and short-term performance of the ultimate composite product. Given the importance of the fibre sizing to the optimisation of the interface, where the silane is the key component for interfacial strength, there is a critical need to improve our understanding of how this region is affected by fibre sizing. This paper focuses on an investigation into the role of a number of silanes typically used in fibre sizings in determining the interfacial shear strength (IFSS) of glass-fibre epoxy composites. The microbond test was used to characterise the effect of the fibre sizing on the IFSS. The work was conducted using silane-coated bare glass-fibres, silane-only sized fibres and fully-sized commercial fibres. It was found that sizing the fibres with silane increased the IFSS (with little significant difference between silanes), more so than with the fully-sized fibres. It was however considered that this apparent increase in IFSS may in fact be as a result of increased fibre tensile strength or an artefact of residual stress and static friction.

1. Introduction

The rapidly growing use of glass-fibre reinforced polymers (GFRP) in a wide range of industries, from automotive to wind turbine applications, means that the demand for development of new and improved composite materials that perform reliably over their lifetime whilst being subjected to high static and dynamic loads over a range of temperatures has never been higher. The fibre-matrix interface region is critical to the mechanical performance of a composite, thus optimisation of the stress transfer capability of this region is extremely important. The fibre sizing is a key parameter for controlling the stress transfer capabilities of the interface but also plays a critical role in defining most of the parameters which influence the long-term composite performance. Given the importance of the fibre sizing to the optimisation of the interface, where the silane is the key component for interface strength, there is a critical need to improve our understanding of how this region is affected by fibre sizing.

Sizings are introduced to bare glass fibres in order to improve their adhesion properties in addition to protecting the fibres from damage and are recognised, in the case of glass-fibres, as a key component in determining success or failure of the reinforcement. Sizings typically consist of primarily-aqueous solutions containing 0.05-10% solids. This solid portion is comprised of a film former (to bind the filaments in a strand and to protect the fibre during processing), a coupling agent (typically silane) to promote adhesion (among other properties such as interphase strength and hydrothermal resistance) and other additives such as anti-static agents, emulsifiers and wetting agents [1]. While the effect of

sizings on composite performance are widely recognized, there is a gap in the knowledge as to *why* they work, beyond the fact that they do.
The present work focuses on examining fully-sized commercial glass-fibres, silane only sized fibres, and bare glass-fibres coated with silane to gauge the effect, if any, on the IFSS when used with a DGEBA-based epoxy resin system and whether any evidence can be presented for the theory that the success of the interface is of as much of a physical nature as it is a chemical one.

2. Experimental

2.1 Materials

The experiments were conducted using a number of boron-free (and one borosilicate) E-glass fibres. Bare (water-sized) and silane-only sized fibres were taken from larger rovings supplied by Owens Corning. Fully-sized commercial fibres (Advantex® SE1500 and SE2020, HiPer-Tex™ W2020) were taken from larger rovings supplied by 3B. The epoxy resin systems used were Araldite® 506 and D.E.R.™ 332 both with triethylenetetramine, technical grade 60%, (TETA) as a curing agent supplied by Sigma Aldrich. Both are bisphenol-A diglycidyl ether-based and the 506 resin also contains a reactive diluent. Owens Corning bare (water-sized) fibres were coated with 1% solutions of γ-glycidyloxypropyltrimethoxysilane (Sigma Aldrich), γ-glycidoxypropylmethyldimethoxysilane (Flurochem) and γ-glycidoxypropylmethyldiethoxysilane (Fluorochem). The fibres used for the investigation are summarized in Table 1.

Table 1: Glass Fibre Summary

Designation	Sizing	Mean Fibre Diameter (μm)
BF	Bare (water-sized)	15.8
APS	γ-aminopropyltriethoxysilane	16.7
GPTMS	γ-glycidoxypropyltrimethoxysilane	16.6
MPTMS	γ-methacryloxypropyltrimethoxysilane	16.4
SE1500	Epoxy-compatible commercial sizing	17.7
SE2020	Epoxy-compatible commercial sizing	18.1
W2020	Epoxy-compatible commercial sizing	19.0
SE1500 AW	SE1500 + acetone wash	17.5
SE2020 AW	SE2020 + acetone wash	18.8
W2020 AW	W2020 + acetone wash	17.9
BF + GPTMS	BF + (γ-glycidyloxypropyl)trimethoxysilane	16.7
BF + GPMMS	BF + (γ-glycidoxypropyl)methyldimethoxysilane	16.4
BF+GPMES	BF + (γ-glycidoxypropyl)methyldiethoxysilane	16.4

2.2 Sample Preparation

For the silane coatings, a pH meter was first calibrated using buffer solutions of pH 4,7 and 10. A dilute acetic acid solution was used to adjust the pH of deionised water to 5-5.5 (5.34) in order to promote hydrolysis of the silane in water. 1mL of silane solution was mixed with 100mL of acidified deionised water (2mL to 200mL Sigma) then left to hydrolyse for 24 hours in a sealed container. Bare (water-sized) glass fibre bundles were completely immersed in the silane solution for 15 minutes then removed and dried in an oven for 15 minutes at 110°C. For the acetone treatments, fully-sized commercial glass fibres were completely immersed in a sealed container of acetone (200mL) for 24 hours then rinsed with clean acetone and left for 24 hours to dry at room temperature.

The epoxy resin and curing agent were mixed to the stoichiometric ratio (≈14pph) and degassed for 10 minutes to remove air trapped during mixing and improve the homogeneity of the mixture. Individual fibres were removed from bundles (in turn removed from the roving) and applied across 20mm gauge length card windows, attached first with double-sided tape then secured with superglue. A length of steel wire (Ø=125µm) was used to apply resin to the fibres in order to form axisymmetric micro-droplets suitable for testing. Each application produced a number of droplets. The wire was touched to the fibre twice for each sample in order to choose the most suitable droplet following optical microscopy. The samples were then cured at 60°C for 1 hour followed by 120°C for 2 hours with a consistent 2°C/min temperature ramp used throughout. Once cured, the droplets were examined under an optical microscope at 200x magnification with ideal, axisymmetric droplets chosen for testing. The fibre diameter, length of the droplet (embedded length) and droplet diameter were then measured. Multiple images were collected for each sample and droplets with diameters of 40-80µm chosen to maintain an approximate droplet size throughout. These measurements are required in order to calculate the IFSS using Equation 1.

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

Where τ is the interfacial shear strength, F_{max} is the maximum load, D_f is the diameter of the fibre and L_e is the embedded length.

2.3 The Microbond Test

A generally accepted manifestation of adhesion is the mechanically measured interfacial shear strength (IFSS)[2]. Over the years a number of experimental techniques have been developed and studied in order to assess the IFSS such as the microbond test and the single fibre pull-out test [3]. It is also known that the IFSS can be influenced by chemicals, such as silane coupling agents. This has in turn led to a number of investigations surrounding both glass and carbon fibre-reinforced polymer composites using the microbond test method [4-5]. In the present work, the effect of various silane coupling agents and full sizings on the IFSS of the composite was investigated using the microbond test. While it is debated whether micromechanical testing methods do in fact provide a true measure of adhesion there can be no doubt that they serve as a useful tool for screening various combinations of fibre and matrix and work as a reliable comparative method.

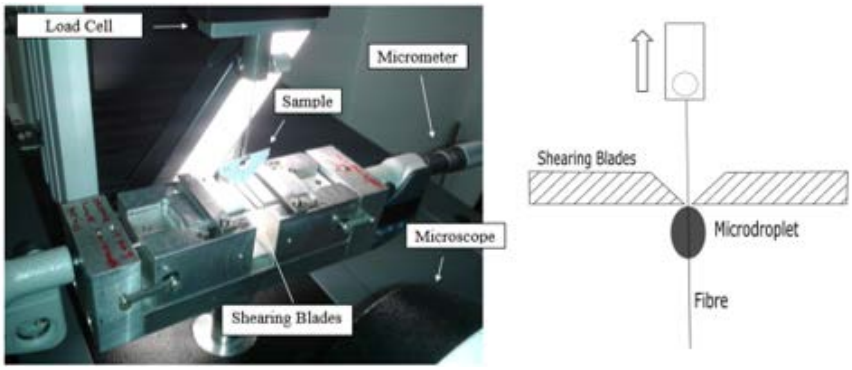

Figure 1: Microbond testing apparatus

Once the samples were prepared, as detailed in 2.2, the microbond test was conducted using an Instron 3342 universal tensile testing machine and a rig designed and built in-house as shown in Figure 1[6]. While microbond testing apparatus varies between labs, the basic principal remains the same. The fibre is able to pass through some aperture freely while the microdroplet is not, resulting in an applied

force and the debonding of the fibre from the surrounding matrix. Once placed in the rig, shearing blades were moved with micrometers in order to secure the sample. Care was taken to avoid damaging or severing the sample prior to testing. The details of the sample were then inputted into the Instron software and the test began at a rate of 0.1mm/min using a 10N load cell. Successful sample debond exhibited a slight curve at the peak force as opposed to a sharp drop in instances of fibre fracture. A further indication of a successful sample was the force beginning to ramp again as a result of frictional forces. Results were excluded for samples where the fibre fractured prior to a successful debond occurring.

3. Results

The microbond testing results was based around three pre-coated silane-only fibres, three commercial fully-sized fibres and three bare glass fibres coated in-house. Of particular interest is the plot of maximum load against embedded area allowing the spread of the data to be easily assessed. Figure 2 shows a typical plot, exhibiting the scatter in data characteristic to the microbond test.

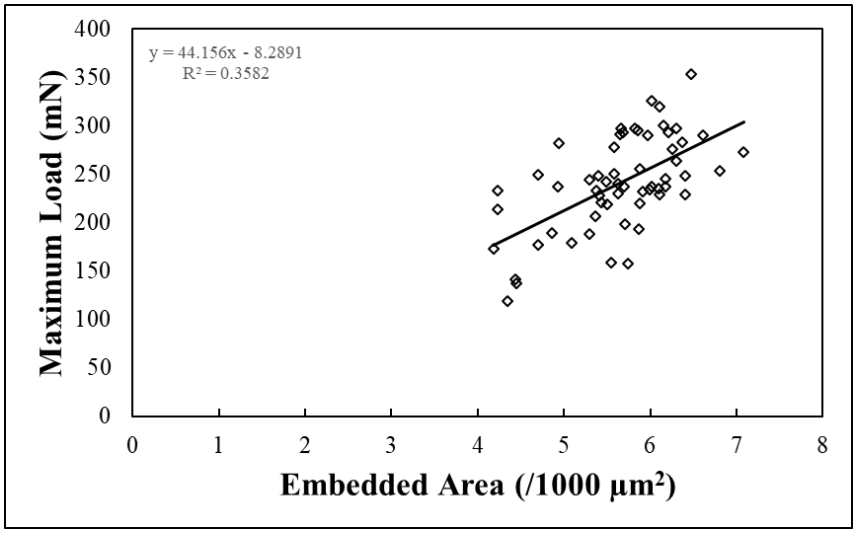

Figure 2: Maximum load vs embedded area for SE1500 with 506 resin

The microbond test results showed that the application of any form of sizing contributed to an improved IFSS compared to a bare fibre. The silane-only sized fibres generally exhibited IFSS in the region of 45 MPa, though there was little significant difference between the various silane coatings. The fully-sized fibres showed lower IFSS results when used with the 506 resin system. When used with the D.E.R. 332 resin system, however, the fully-sized fibres performed better than any silane-only sized fibre.

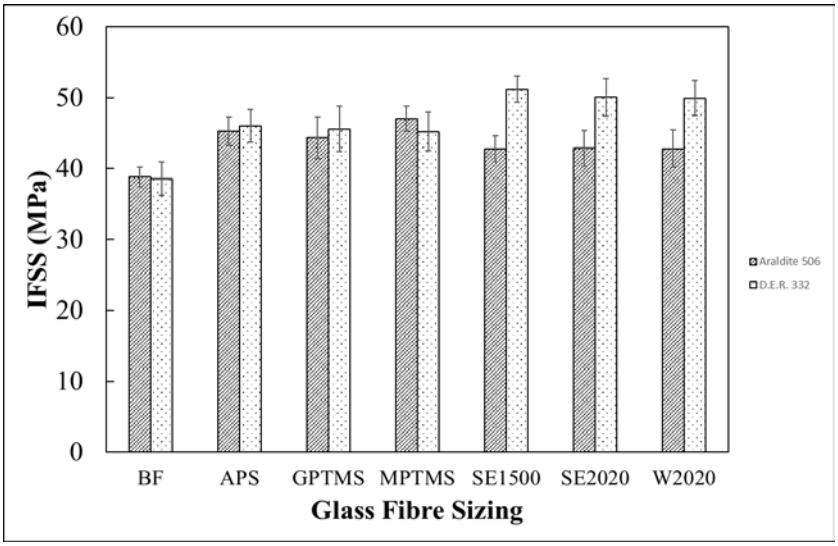

Figure 3: Comparison of glass fibre sizings

Following treatment with silane, each of the fibres showed increased IFSS over bare glass fibres. The fibres which were coated with GPTMS in-house showed comparable results to those which were received pre-coated. There was little significant difference (within confidence limits between) GPTMS and GPMMS with GPMES exhibiting improved results for both resin systems.

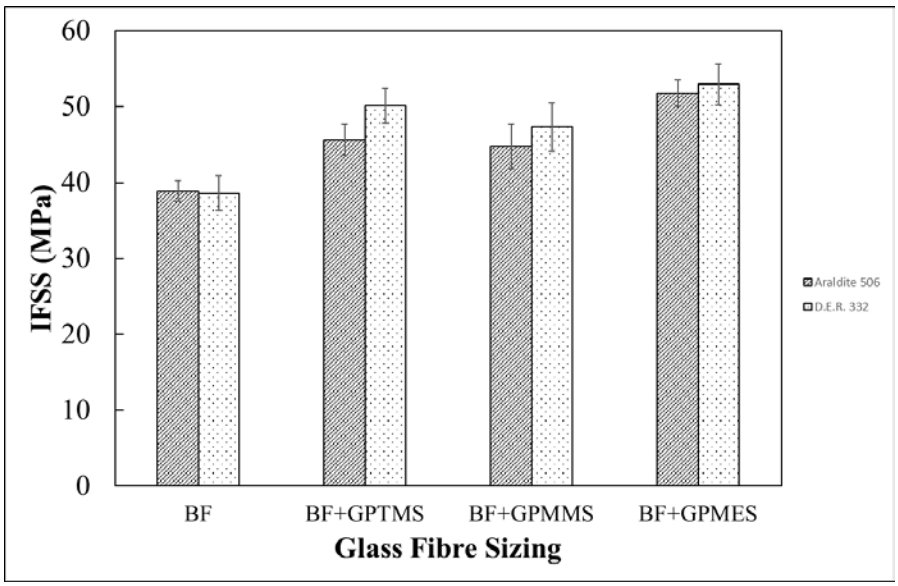

Figure 4: Comparison of bare glass fibres before and after treatment with silane

Following treatment in acetone for 24 hours, the IFSS of the commercial fibres was improved by approximately 8MPa.

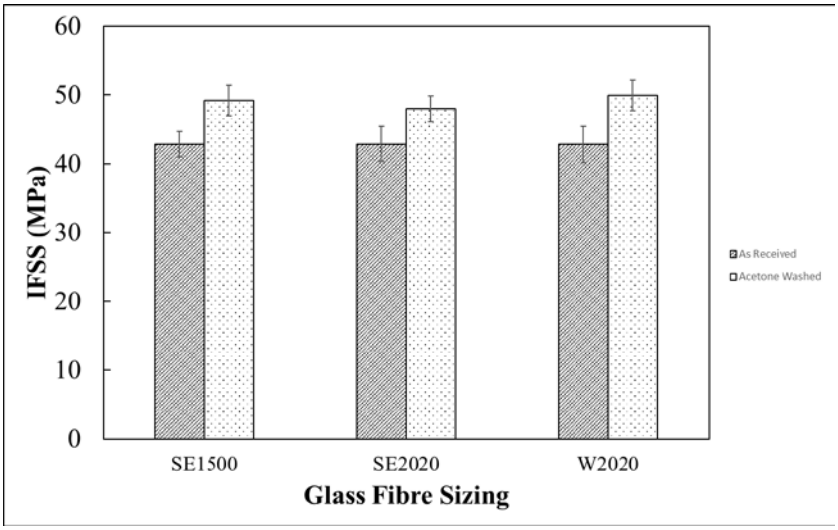

Figure 5: Comparison of fully-sized fibres following acetone treatment

The microbond testing results are summarised in Table 2:

Table 2: Summary of Microbond Testing Results

Designation	τ(MPa) 506	95% Confidence	τ(MPa) 332	95% Confidence
BF	38.9	1.4	38.6	2.3
APS	45.3	2.0	46.0	2.3
GPTMS	44.4	2.9	45.6	3.2
MPTMS	47.1	1.7	45.2	2.7
SE1500	42.8	1.9	51.2	1.9
SE2020	42.9	2.5	50.1	2.7
W2020	42.8	2.6	49.9	2.4
SE1500 AW	49.2	1.9	-	-
SE2020 AW	48.0	2.5	-	-
W2020 AW	50.0	2.6	-	-
BF + GPTMS	45.6	1.9	50.1	3.3
BF + GPMMS	44.8	2.3	47.3	2.9
BF+GPMES	51.8	2.2	53.0	3.1

4. Discussion

It is evident that the application of silane, or in fact *any* sizing, increases the interfacial tenacity of the composite. Given that there is little significant difference between the silane coatings, it is reasonable to suggest that the improvement may be of a (at least partially) physical nature as much as a chemical one. It would be expected that sizings (commercial and GPS-based) formulated to give improved results with epoxies (thus containing reactive groups) would give uniformly improved performance, though this was not always the case. In addition to chemical interactions, it is important to consider the physical interactions that may contribute to a proportion of the measured IFSS.

Figure 6 shows SEM images of micro-droplet samples exhibiting a pocking or deformation of the surface as a result of shrinkage during curing.

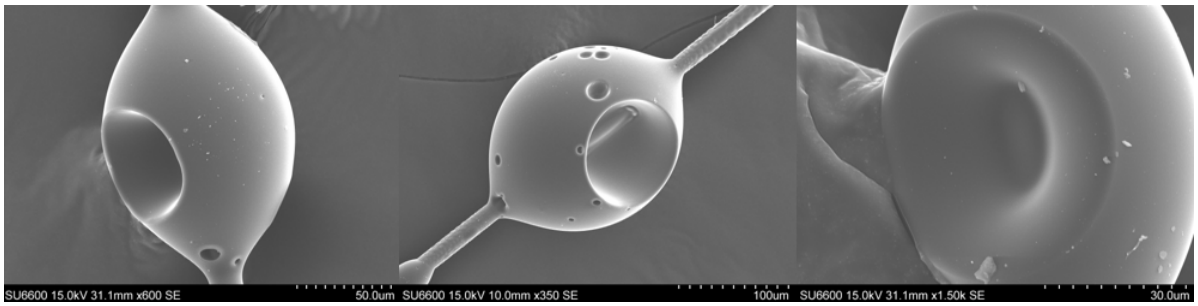

Figure 6: SEM of micro-droplet cure shrinkage

This dimensional shrinkage can result in radial compressive stresses "gripping" the fibre. In addition, static friction may be increased through the application of a silane/sizing compared to bare glass. In their review of the literature Kalantar and Drzal found that Aramid showed improved interfacial properties following a roughening of the surface, though it would be interesting to study this further in regards to glass-fibre/epoxy composites [7].

When used with the Araldite 506 epoxy, the fully-sized fibres exhibited marginally weaker interface properties than that of the silane-only sized fibres. It is possible that the acetone treatment removes additives that, while essential for processing and production, may also in fact detract from the interfacial properties of the composite.

While the results for both resin systems remained more or less consistent for the pre-coated silane-only fibres, the D.E.R. 332 resin system exhibited superior IFSS when used in conjunction with commercially-sized fibres and with those coated in-house. Both epoxy resins are of the DGEBA, with the Araldite 506 containing a reactive diluting agent and D.E.R. 332 being a single resin. In general, the viscosity of the D.E.R. resin resulted in slightly larger droplets that, while still within the imposed 40-80µm diameter limit, resulted in a slightly larger embedded area.

Though there is debate on whether micromechanical testing methods are realistic approximations of the *true* interface of the composite, the microbond test (among others) remain effective methods for screening and comparing various sizings and allow for almost any fibre and matrix combination to be used[8-9].

5. Conclusions

The effect of coating glass fibres with silane coupling agents was quantified using the microbond test. It is clear that the application of a silane increases the IFSS though there may be a number of reasons why this may occur. Conventional wisdom would suggest that the addition of silane resulting in the improvement is of a chemical nature, arising as a result of silane reacting with the matrix components during thermosetting. That there is little difference in the results between the silanes formulated specifically for use with epoxy and those that are could suggest that the phenomenon may instead be of a physical nature. Reilly and Thomason showed that silane sizings considerably improved the strength of glass-fibres, attributing the increase to a possible "healing" of surface flaws on the glass [10]. As microbond results where the fibre fractures prior to the microdroplet successfully debonding, it can be proposed the IFSS of sized fibres is increased as a result of fewer instances of fibre fracture and the ability to apply greater loads. Bare glass samples are limited by their tensile strength. If they were ever to have IFSS values in the range of some of the high-performing results, the fibre would have fractured long before the droplet could debond. Further arguments for the physical nature of the

apparent IFSS involve cure shrinkage of the droplet "gripping" the fibre, with thermal residual stress and static friction contributing to a significant portion of the measured IFSS [11-12].

Further lines of research into this area such as tensile testing of all the fibres involved would be beneficial to draw a correlation between fibre tensile strength and IFSS. Of particular interest is the acetone washed commercial fibres and whether they exhibit a noticeable depreciation in strength following the treatment. Further work will also involve isolating the fibre surface through the application of an inert coating prior to applying resin micro-droplets.

Acknowledgments

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