

## INVESTIGATING THE EFFECT OF SILANE COUPLING AGENT ON GLASS FIBRE/THERMOPLASTIC INTERFACIAL ADHESION

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**Abstract:** *Fibre coating (sizing) is a key component for controlling interface integrity and functionality, as well as governing long-term performance characteristics of glass fibre composites. Silane coupling agent is the crucial component in glass fibre sizing contributing to interfacial adhesion, and its role needs to be fully understood in order to develop efficient sizing formulations. This study investigates the effect of a number of different silanes, typically used in glass fibre sizings, on the interfacial shear strength (IFSS) when combined with different thermoplastic polymers. IFSS was measured using the microbond test for both bare and silane sized glass fibres. The results showed that IFSS increased by sizing the fibres with silane. This improvement was observed for Polypropylene (PP) in all the applied silanes, whereas maleic anhydride grafted polypropylene (MaPP), polyamide 6 (PA6) and polybutylene terephthalate (PBT) did not show significant improvement in some of the applied silanes.*

**Keywords:** Microbond, Interface, Silane, Glass Fibre, Thermoplastics

### 1. Introduction

Glass fibre reinforced polymers are the most widely used polymeric composites due to the specific mechanical characteristics and low cost of glass fibre. In recent years, the development and applications of fibre-reinforced thermoplastic polymer composites have increased in different industries such as automotive and aerospace. Glass fibre thermoplastic composites are emerging technology that is being researched significantly these days as they usually exhibit a higher range of toughness and recyclability and have less complex processing requirements in comparison with thermosets [1].

Fibre, matrix, and the fibre–matrix interface properties are important parameters affecting the thermoplastic composites properties. To have desirable composite properties, the fibre-matrix interface should have the ability to effectively transfer stresses across the interface. During manufacturing of glass fibre, a thin surface coating (called Sizing) of mainly polymeric materials is applied on the surface of fibre. Sizing is a key component for controlling the interface integrity and functionality of glass fibre thermoplastic composites.

Organofunctional silanes are key components of sizing, which are usually referred as coupling agents. These silanes are reported to improve the interfacial strength and hydrothermal resistance of the interface [2]. The general structure for a silane coupling agent is  $[X-Si(OR)_3]$ , where R is a methyl or ethyl group and X is a chemically reactive group that can interact with the composite matrix and/or the film former [2]. The interaction is usually known to be a chemical one, where the matrix is a thermoset polymer and the X group on the silane reacts with the matrix elements. It is not well understood whether a high molecular weight thermoplastic polymer matrix would have the same chemical interaction [3]. There are only a few studies on interfacial properties on glass fibre thermoplastics compared to glass fibre thermosets [3].

This study investigates the effect of a number of different silanes typically used in glass fibre sizings, namely  $\gamma$ -aminopropyltriethoxysilane (APS),  $\gamma$ -glycidoxypropyltrimethoxysilane (GPS) and  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS), on the interfacial shear strength (IFSS) when combined with different thermoplastic polymers. Microbond testing, which is a widely accepted method in polymer composites research has been used to evaluate the IFSS [4]. Microdroplets have been created from different thermoplastics i.e., PP, MaPP, PA6, PBT on unsized and silane sized glass fibres. The significance of the averaged IFSS for the investigated systems is evaluated by two-tailed Student's T-Test [5]. An example of SEM observations of debond fibre matrix is illustrated. Furthermore, compatibility of the thermoplastics with different silane sized fibres is reported and discussed.

## 2 Materials and method

### 2.1 Materials

The experiments were conducted using E-glass fibres. Bare fibre (water-sized) was taken from a large roving supplied by Sisecam. The thermoplastic polymers used were, PP (PETOPLen EH102), MaPP (Polybond<sup>®</sup> 3200), PA6 (Tecomid<sup>®</sup> NB40 NL) and PBT (Tecodur<sup>®</sup> PB30 NL) supplied by Petkim, Addivant and Eurotec respectively. APS, GPS and MPS were purchased from Sigma Aldrich. The bare fibres were coated with 1% solutions of APS, GPS and MPS. The silane sized fibres used for the investigation are summarized in Table 1.

Table 1: Glass fibre summary.

Designation	Sizing	Mean fibre diameter ( $\mu\text{m}$ )
BF	Bare (water size)	17.5
APS	$\gamma$ -aminopropyltriethoxysilane	17.7
MPS	$\gamma$ -methacryloxypropyltrimethoxysilane	18.6
GPS	$\gamma$ -glycidoxypropyltrimethoxysilane	17.9

### 2.2 Silane treatment

The process of applying the silane coatings started with calibrating a pH meter using buffer solutions of pH 4, 7 and 10. For adjusting the pH of deionised water to 5-5.5, a dilute acetic acid solution was used. This is to promote hydrolysis of the GPS and MPS in water. 1 mL of silane was mixed with 100mL of acidified deionised water then left to hydrolyse for 24 h in a sealed plastic container (Figure 1). APS solution was made at pH 7, as that's the optimised pH level for APS [2]. 30 cm BF bundles were completely immersed in the silane solutions, as shown in Figure 1 for 15 minutes, then removed and dried in an oven for 30 minutes at 110°C.



Figure 1. Silane solution (left), immersed fibre bundles in the silane solution (right)

## 1.2 Microbond test

Sample preparation was done similar to a previous publication by Nagel et al. [6]. Steel washers were employed as the sample holders for the microbond test. Individual fibres were removed from bundles and applied on a steel washer, attached first with double-sided tape then secured with superglue. Long fibres were extruded from thermoplastics pellets and then they were used to make a knot around the fixed glass fibre on the washer. The samples were then proceed at 220°C for PP, 200°C for MaPP and 260°C for PA6 and PBT in a vacuum oven under nitrogen flow and left to reach the ambient temperature under nitrogen. The droplets were examined under an optical microscope (200x). Only axisymmetric droplets were chosen for the test. Figure 2 shows an example of a fine PP droplet that is prepared for the test. The fibre diameter, length of the droplet (embedded length) and droplet diameter were measured using the image processing software package ImageJ. A total of 30 samples were prepared for each batch and were subjected to microbond test using an Instron 3342 universal tensile testing machine as shown in Figure 4. The droplet was brought to just below the blades and the blades were closed until touching the fibre. 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. Eq. (1) formulates the calculation method for the IFSS.

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

Where  $\tau$  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.

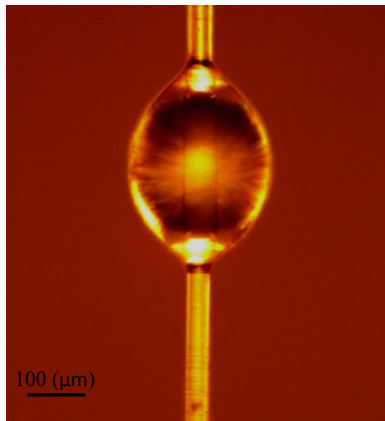


Figure 2. An example of a PP droplet

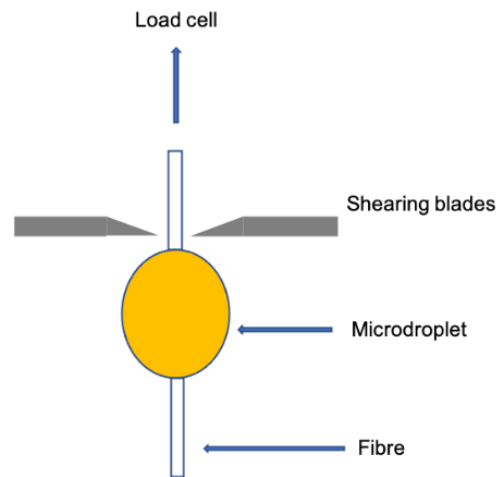


Figure 3. Microbond set up

### 3. Results and discussions

Although it is not fully accepted whether micromechanical testing methods provide realistic approximations of the true interfacial properties, the microbond test is widely used by many researchers as an effective method for screening and comparing various sizings and it allows testing almost any combination of fibre and matrix [7, 8].

The microbond testing results were based around bare and three different silane coated fibres (APS, GPS, MPS) with four different thermoplastics. The plot of maximum load against embedded area provides information on the spread of the data to be easily assessed. Figure 4 shows a typical plot, exhibiting the scatter in data characteristic in the microbond test.

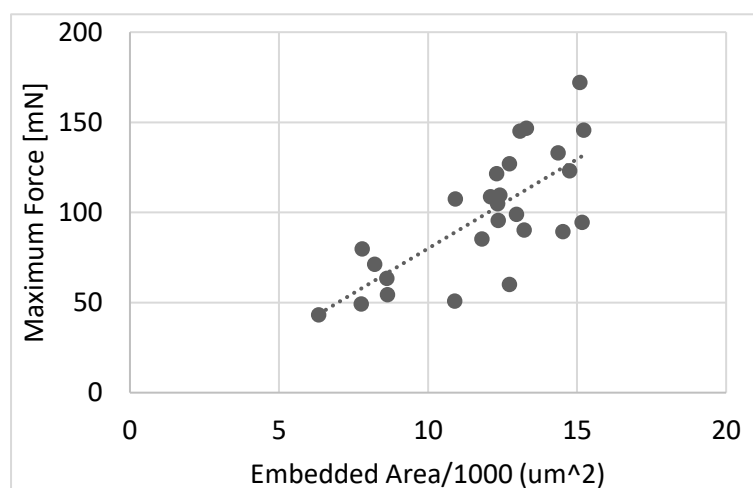


Figure 4. Maximum load vs embedded area for APS with PP matrix.

Figure 5 shows the IFSS results obtained by the microbond tests on PP, MaPP, PA6 and PBT systems. All the IFSS and Student T.test results are also summarized in Tables 2 and 3. Overall, the PBT system has the highest IFSS values of all the investigated fibre/matrix systems. MaPP has the second highest IFSS value, followed by PA6 and PP.

For PP systems, the application of any form of sizing contributed to an improved IFSS compared to a bare fibre. The silane sized fibres generally exhibited IFSS in the region of around 8 MPa, which shows the improvement in IFSS compared to BF. The p values obtained from the two-tailed Student's T-Test, see Table 3, between Bare and Silane sized fibres show that the difference in average apparent IFSS values for these systems are significant at the 95% confidence level, while there is a small difference when comparing the silane sized fibres with each other.

It can be seen that IFSS for MaPP systems are much higher than PP systems for BF and silane sized fibre, this is in agreement with previous observation by Nygård et al. [9]. The results show that APS had the highest IFSS value of 21.9 MPa among all the samples in the MaPP system, and there is a little difference between the MPS and GPS. The T.test results in Table 3 also certifies these results.

The IFSS results for PA6 systems show that APS has the highest IFSS value of 19.8 MPa, whereas Bare and GPS has the lowest value 16.7 MPa and 17.1 MPa respectively. However, the T.test results indicate that the differences in average apparent IFSS values for these batches are not significant.

Microbond results for PBT systems stand as the highest value (approximately 30 MPa for BF and MPS, and 32 MPa for APS and GPS) among all the systems. However, there is only a small improvement in silane sized fibres compared to BF.

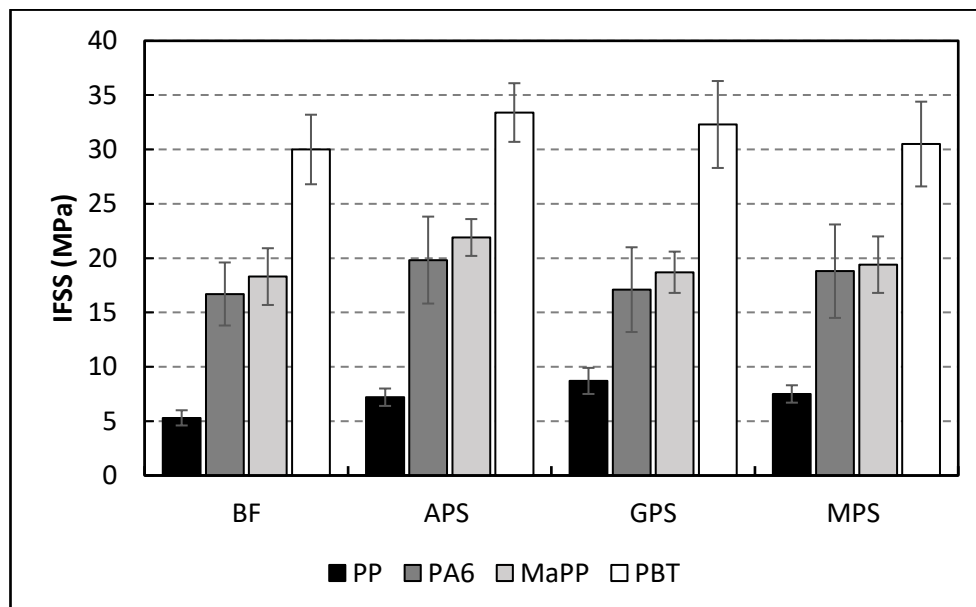


Figure 5. IFSS results for the investigated systems.

Table 2. Summary of Microbond Testing Results

Designation	IFSS (MPa)	IFSS (MPa)	IFSS (MPa)	IFSS (MPa)
	PP	MaPP	PA6	PBT
BF	5.1±0.6	18.3±2.6	16.7±2.9	30.0±3.5
APS	7.2±0.8	21.9±1.7	19.8±4.2	31.9±3.9
GPS	8.7±1.2	18.7±1.9	17.1±4.3	32.3±4.5
MPS	7.5±0.8	19.4±2.6	18.8±4.9	30.5±3.7

Table 3. Two-tailed Student's t-Test between Bare and Silane sized fibres

Paired samples	p value in different Thermoplastic systems			
	PP	MaPP	PA6	PBT
BF/APS	0.003*	0.02*	0.30	0.29
BF/GPS	0.0002*	0.82	0.82	0.28
BF/MPS	0.0006*	0.29	0.43	0.60
APS/GPS	0.07	0.005*	0.27	0.89
APS/MPS	0.62	0.14	0.74	0.59
GPS/MPS	0.12	0.16	0.51	0.53

\* Significant at 0.05 level, 95% confidence limit

From the results, the application of silane has some improvement in the IFSS of the thermoplastic composites. Given that there is not a significant difference between the IFSS results using different silane sizing, it is reasonable to suggest that the improvement might be due to both physical and chemical bonds in the interface.

Figure 8 shows SEM images of the debond PP micro-droplet sample. The SEM observations confirm the validity of the test, as the debonding can be seen clearly without any damage to the matrix or fibre.

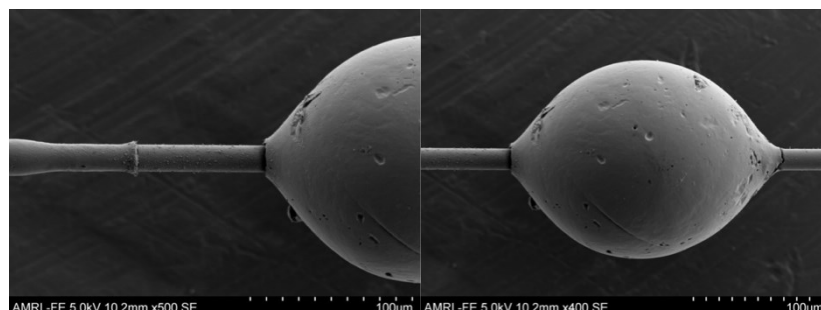


Figure 8. SEM image of debond PP droplet.

#### 4. Conclusion

This study investigated the effect of different silane coatings and the adhesion of glass fibres with different thermoplastic matrices including PP, MAPP, PA6 and PBT. The microbond test was used to evaluate the effectiveness of silane coupling agents for coating glass fibres to improve the interfacial properties. In addition, SEM observation was used to study the morphology of the debonded droplets. SEM observations revealed the successful nature of debond, confirming the test accuracy. In most of the studied polymers, silane only increased average IFSS by small amounts which were generally not significant at 95%CL. There were some exceptions as IFSS improved for PP in all the silane sized fibres and MaPP in APS sized fibres. Previous studies suggest that this increase might be associated with the improvement of a chemical bond because of silane reacting with the matrix components. However, the IFSS increase observed in this study may instead be of a physical nature as the increase in the IFSS does not significantly vary by changing the matrix-reactive group on the silane. This conclusion needs to be supported with more technical analysis to better understand the bond nature to pave the way towards improved glass fibre reinforced thermoplastic materials. As a result, it is suggested that further analysis such as surface morphology measurement using atomic force microscopy and surface energy evaluation using contact angle measurements are required to carefully differentiate the contribution of physical and chemical nature of interfacial bonds.

#### Acknowledgements

The authors would like to extend thanks to Şişecam company and the University of Strathclyde as the sponsors of this project.

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