

A Review of the Current Industrial Methods of Selecting Interfacial Coupling Agents to Enhance the Mechanical Performance of Short Fibre-Polymer Composites

M. Hayward*, J. Johnston*, T. Dougherty** and K. de Silva***

*Victoria University of Wellington, School of Chemical and Physical Sciences,
PO Box 600, Wellington, New Zealand, matilda.hayward@vuw.ac.nz

**Nuenz Limited, Lower Hutt, New Zealand

***Product Accelerator, University of Auckland, New Zealand

ABSTRACT

Coupling agents are used in fibre-polymer composites to enhance the dispersion and adhesion of the fibres and to maximise the composite's mechanical performance. This paper aims to review the existing approaches of selecting a coupling agent which will maximise the dispersion of randomly-oriented, discrete fibres in thermosetting polymer composites. Specialist insight, industrial sizing tables and trial-and-error testing are typical techniques currently used to select a coupling agent for a novel composite. The volume of potential coupling agents and the ambiguity in the sizing tables has made selecting the optimum coupling agent a current problem facing the composites industry.

In this work, a range of functionalised Si₃N₄-fibre polymer composites was synthesised using a variety of silane coupling agents (SCAs) and commercial thermoset polymer resins. The tensile strength, Young's modulus, toughness and shore D hardness of the composites were measured. It was determined that changing the SCA at the interface had a significant effect on the overall performance of the composite. Microstructural analysis of the interface was used to draw conclusions about the influence of the SCA on the extent of adhesion across the fibre-polymer phase boundary.

The measured trends in composite tensile strength values were compared to the suggestions from typical sizing tables for each polymer to determine the effectiveness of the primary method used for selecting an SCA. There was a significant amount of deviation between the SCAs predicted to couple to the resin and the SCA which resulted in the greatest increase in tensile strength. It was concluded that current SCA selection methods are not efficient or robust techniques to develop a novel composite with maximum mechanical properties.

Keywords: polymer composites, interfacial adhesion, sizing tables, mechanical performance, fibre-polymer composites, coupling agents, dispersion

1 INTRODUCTION

The mechanical properties of a fibre-polymer composite are largely determined by the extent of fibre dispersion and the strength of interfacial adhesion across the fibre-matrix phase boundary. [1] SCAs are widely used throughout the

composites industry to treat the surface of fibres to enhance dispersion, improve interfacial adhesion and to optimise the material's mechanical properties. [2] There is a large range of SCAs with different functional end groups which can be tailored to couple to a polymer resin.

Selecting which SCA best interacts with a polymer resin is a current problem facing the composites industry. Typically, industrial sizing tables, shown in Table 1, are the primary source of information used to select a suitable coupling agent for a polymer composite.

SCA \ Resin	Vinyl	Epoxy	Methacryloxy	Acryloxy	Amino	Ureide	Mercapto	Isocyanate
Melamine		*			*			*
Phenolic		*			**	*	*	*
Epoxy		*			**		*	*
Urethane		*			*	*	*	**
Polyimide		*			*	*		*
Polyester	*	*	**	**				

* = Effective at coupling ** = Very effective

Table 1. Typical sizing table for SCAs. [3]

Industrial sizing tables are generic, vague guides which vary depending on the source. [3–5] Typically, 3 - 5 coupling agents are suggested per polymer resin. Therefore, composite manufacturers need to conduct trial-and-error experimentation on at least four different SCAs to determine which is the most effective at producing an advanced composite material with superior mechanical properties.

Due to the number of additional, unknown components in commercial polymer resins, the suggested coupling agents can be ineffective for coupling across a composite interface, or the most effective SCAs may not be recommended.

An additional challenge for composite manufacturers is that selecting the wrong coupling agent can be detrimental to the mechanical performance of the composite. Expensive and time-consuming trial-and-error experimentation is required to find a functionalisation technique which is best suited for a fibre-polymer composite.

This work compares the influence of a variety of silane coupling agents on the mechanical performance of fibre-

polymer composite materials. The effectiveness of using the provided sizing tables to determine which SCAs onset the best mechanical property improvements is examined and any disparities are discussed.

2 EXPERIMENTAL

The silane coupling agents used in this study were (3-aminopropyl)triethoxysilane (APS), vinyltrimethoxysilane (VMS), provided by Sigma Aldrich, New Zealand, (3-glycidyloxypropyl)trimethoxysilane (GPS), [3-(methacryloyloxy)propyl]trimethoxysilane (MPS), bis[3(triethoxysilyl)propyl] tetrasulfide (SCA98), triethoxy(3-thiocyanatopropyl)silane (SCA984) and (3-mercaptopropyl)triethoxy silane (SCA989) provided by Strukol Company of America, USA.

WestSystem epoxy (WS) was a WestSystem 105 epoxy polymer resin and WestSystem 206 slow amine hardener, supplied by Adhesive Technologies, Auckland. Toughened epoxy (TEp) was a ‘Polyline AP L312E’ resin provided with an aliphatic amine ‘Polyline AP L312E’ hardener by the Polymer Group, Auckland. Vinyl ester (VE) was a ‘Derakane 411-350’ epoxy vinyl ester resin and was supplied with a methyl ethyl ketone peroxide catalyst by Adhesive Technologies, Auckland. SilCrete resin (Silc) was ‘SilCrete TSL’; a two-component polyurethane silicate spray thin skin liner (TSL) provided by Polymer Group Ltd, New Zealand.

Silicon nitride fibres (>95 % α -Si₃N₄) were provided by Nuenz Limited, New Zealand, and had lengths of 8 - 24 μ m and diameters of D50 = 0.3 μ m. All solvents and reagents used in these experiments were of analytical reagent grade at \geq 99 % purity.

Si₃N₄ fibres were functionalised with the SCAs using the methods outlined in previous work. [6] All composites in this study were made up at 0.08 vol.% fibre loadings. The fibres were mixed into the resin component of each two-part polymer and dispersed using a ball-mill tumbler for 6 h. The hardener was added to the resin at a ratio suggested by the resin supplier and was thoroughly mixed before being poured into moulds and left to cure for 24 – 48 h.

Tensile tests were carried out using an Instron 3367, and the tensile specimens were made according to the D3039 ASTM Standard. Tensile samples were dog bone shaped, with gauge length, width and thickness of 98, 15 and 5 mm, respectively. Various strain rates were used depending on the type of polymer material used: WS and VE composites had a strain rate of 1.5 mm min⁻¹, TEp composites were at 2.0 mm min⁻¹ and Silc composites were at 3.0 mm min⁻¹. The ultimate tensile strength (UTS), Young’s modulus (E_M) and toughness (U_T) were all determined from the tensile stress-strain curves. Shore hardness measurements were taken using an industrial Shore durometer (scale D) according to ASTM D2240 standard. Shore hardness samples were circular disks which were 30 mm in diameter and 10 mm thick.

SEM was performed on the fracture surface of the composites using a JEOL 6500F field emission gun at 20 kV accelerating voltage. The sample surfaces were pre-coated with a 24 nm thick layer of carbon using a JEOL JEC-560 carbon coater.

3 RESULTS AND DISCUSSION

3.1 Epoxy Composites

Table 1. suggests that amino-based coupling agents onset very effective coupling to epoxy resins, and epoxy, mercapto and isocyanate-based coupling agents will couple effectively. From Table 1. it can be predicted that APS will produce the epoxy composite with the best mechanical properties and GPS and SCA989 will enhance an epoxy composite’s mechanical performance to some extent.

The UTS of the SCA-Si₃N₄-WS composites were measured to determine which SCA onset the greatest improvement in mechanical performance and the results are presented in Table 2. The Young’s modulus, toughness and hardness of the composites are also presented to confirm that the trends in UTS values are consistent across other mechanical tests.

SCA	Mechanical Properties				
	UTS (MPa)	% Incr.	E _M (MPa)	U _T (MPa)	Shore D
Blank	37(2)	-	22(2)	44(5)	74.3(5)
GPS	43(4)	16	25(1)	63(9)	81.1(6)
APS	39(4)	5	23(1)	59(9)	76.6(4)
VMS	36(3)	-3	21(1)	41(6)	76.1(8)
SCA98	35(3)	-5	21(1)	44(7)	75.1(4)
Si ₃ N ₄	34(2)	-8	21(2)	44(8)	75.8(8)
SCA984	33(4)	-11	21(2)	42(9)	77.2(4)
SCA989	32(3)	-14	20(1)	32(5)	77.6(5)
MPS	31(3)	-16	20(1)	35(5)	75.6(6)

Table 2. Mechanical analysis of the WS composites.

Table 2. shows that GPS and APS onset significant improvements to the composites UTS with a 16 % and 5 % increase, respectively. It was predicted that APS would be the most effective at coupling to an epoxy. However, the UTS of the APS composite was 10 % lower than that of the GPS composite. SCA989 contains a mercapto group which was predicted to couple effectively to an epoxy. However, SCA989 resulted in a 14 % decrease in UTS compared to the neat WS resin. These results show that the sizing tables do not accurately predict which SCA will onset the best improvements in an epoxy composite.

SEM analysis of the fractured composite surface was used to analyse the interfaces of the composites with the highest and lowest UTS values. The SEM images of GPS- and MPS-Si₃N₄-WS composites are shown in Figure 1.

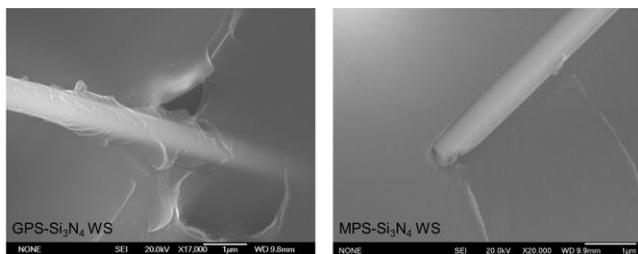


Figure 1. SEM of GPS- and MPS-Si₃N₄-WS composites.

The SEM images in Figure 1. show that the GPS-functionalised fibres, which resulted in the composite with the highest UTS, had a thick layer of polymer coating over the surface of the fibres. The coating shows good adhesion across the fibre-polymer interface. The MPS-functionalised fibres had an interfacial gap between the fibre and the polymer matrix suggesting poor interfacial adhesion. The reduced adhesion at the interface explains the reduction in composite UTS for the MPS-Si₃N₄-WS composite.

The trends between the different SCAs and the UTS of the epoxy composites were compared for TEp, a different commercial epoxy resin. The UTS values for the SCA-Si₃N₄-TEp composites are presented in Table 3. alongside the Young's modulus, toughness and shore D hardness.

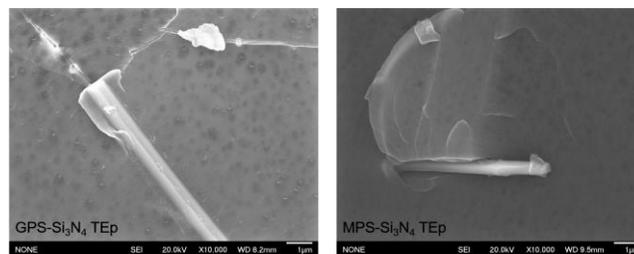


Figure 2. SEM of GPS- and MPS-Si₃N₄-TEp composites.

The SEM images in Figure 2. confirm that composites with the greatest adhesion across the fibre-polymer interface correlated to the composites with the highest enhancements to the composites mechanical properties, with GPS-Si₃N₄-TEp showing good bonding to the fibres and MPS-Si₃N₄-TEp showing poor bonding.

These results show that two resins of the same type can interact differently with a coupling agent. Therefore, a generic prediction of which SCAs will perform best for a resin type is not an efficient or effective method for selecting a coupling agent to maximise the mechanical performance of a polymer composite.

3.2 Vinyl Ester Composites

Table 1. suggest that for a vinyl ester resin, methacryloxy and acryloxy based SCAs will produce the composite with the greatest adhesion. Vinyl and epoxy based SCAs are also predicted to couple effectively. Table 1. predicts that MPS- Si₃N₄-VE will have the highest UTS and the VMS- and GPS-functionalised composites will also have improved properties.

The UTS values for the SCA-Si₃N₄-VE composites are presented in Table 4. alongside the Young's modulus, toughness and shore D hardness.

SCA	Mechanical Properties				
	UTS (MPa)	% Incr.	E _M (MPa)	U _T (MPa)	Shore D
Blank	58(3)	-	17(1)	148(20)	74.6(6)
GPS	63(2)	9	19(1)	176(14)	80.2(4)
VMS	61(4)	5	19(1)	177(16)	81.3(4)
Si ₃ N ₄	60(3)	3	19(1)	167(15)	77.6(7)
APS	59(3)	2	18(2)	144(14)	77.2(5)
SCA984	59(4)	2	19(1)	139(12)	77.9(9)
SCA989	58(3)	0	18(1)	158(18)	75.1(6)
SCA98	58(3)	0	18(1)	133(16)	74.4(6)
MPS	57(3)	-2	18(1)	157(19)	75.8(9)

Table 3. Mechanical analysis of the TEp composites.

Table 3. shows that GPS and VMS onset the highest increase in UTS with a 9 % and 5 % increase compared to the blank TEp, respectively. Table 1. accurately predicted that GPS would couple effectively to epoxy resins. However, the sizing table did not suggest that the vinyl group in VMS would onset improvements to the epoxy composite. APS was predicted to couple very effectively to the resin. However, the APS-Si₃N₄-TEp composites only increased the UTS by 2 % compared to the neat TEp, which was less than the addition of unfunctionalised fibres which correlated to a 3 % increase. SCA989 did not favourably enhance the properties of the composite, despite being predicted to couple effectively. These results further demonstrate the lack of reliability in the predictions from industrial sizing tables.

The SEM images of GPS- and MPS-Si₃N₄-TEp composites are shown in Figure 2.

SCA	Mechanical Properties				
	UTS (MPa)	% Incr.	E _M (MPa)	U _T (MPa)	Shore D
Blank	25(1)	0	16(1)	28(7)	74.9(9)
APS	33(3)	32	18(1)	53(8)	79.8(1)
VMS	33(4)	32	18(1)	40(4)	80.9(2)
SCA98	32(3)	28	18(1)	45(7)	81.1(5)
GPS	29(2)	16	18(1)	33(5)	80.0(5)
SCA989	29(2)	16	17(1)	35(6)	77.5(6)
SCA984	29(3)	16	18(1)	37(6)	76.2(4)
MPS	28(3)	12	17(1)	31(5)	77.5(6)
Si ₃ N ₄	26(3)	4	16(1)	30(7)	79.0(6)

Table 4. Mechanical analysis of VE composites.

Table 4. shows that APS and VMS produced the highest increase in UTS with a 32 % increase compared to blank VE, although APS was not suggested as an effective coupling agent for VE in Table 1. MPS, which was predicted to produce the composite with the greatest increase in mechanical properties, only resulted in a

comparatively marginal UTS improvement of 12 %, which was lower than any other coupling agent.

The VE composites with the highest and lowest UTS values were APS- and MPS-Si₃N₄-VE, respectively and the SEM images are shown in Figure 3.

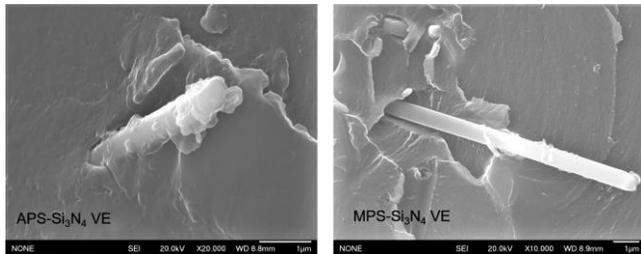


Figure 3. SEM of APS- and MPS-Si₃N₄-VE composites

The SEM images in Figure 3. show that the APS-functionalised fibres had good adhesion between the fibre and the polymer matrix as the resin remained well bound to the fibre surface during the fracture process. The MPS-Si₃N₄-VE composites had a gap separating the fibre and polymer indicating poor interfacial adhesion.

These results show that while the suggested SCA from a sizing table may result in an increase in composite strength, it is possible that another SCA can increase the composite's properties by a greater extent.

3.3 Polyurethane Composites

Table 1. suggests that a urethane-based polymer resin will react well with epoxy-, amino- and mercapto-based coupling agents. This suggests that GPS, APS and SCA989 will couple effectively to the fibre surface and the polymer matrix and produce the composite with the best mechanical properties.

The UTS values of the SCA-Si₃N₄-Silc composites are presented in Table 5. The Young's modulus, toughness and hardness of the composites were also measured to confirm that the trends in UTS values are consistent across other mechanical tests.

Table 5. shows that, as predicted by the sizing tables, GPS, APS and SCA989 produced the highest increase in mechanical properties with a 12 %, 5 % and 3 % increase in UTS compared to the blank Silc, respectively.

The SEM images of the Silc composites could not be presented due to proprietary reasons.

4 CONCLUSION

This work aimed to review the current methods for selecting a coupling agent to enhance the dispersion and adhesion of fibres in a polymer composite and determine how effective and efficient they are.

The mechanical properties of SCA-Si₃N₄-polymer composites were measured for a variety of SCAs and common thermoset polymer resins. It was found that changing the SCA at the fibre-polymer interface had a significant effect on the composite's mechanical performance. The trends in UTS values were compared to the suggestions from industrial sizing tables. It was found that the SCAs which were predicted to produce the composites with the highest properties often underperformed and occasionally, the best composites were formed using SCAs that were not recommended by the sizing tables. It was concluded that the current generic methods to predict which SCA will produce the maximum composite properties are typically ineffective and a new predictive model needs to be developed.

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SCA	Mechanical Properties				
	UTS (MPa)	% Incr.	E _M (MPa)	U _T (MPa)	Shore D
Blank	10.2(3)	0	4.7(1)	20(2)	59.2(4)
GPS	11.4(8)	12	5.1(2)	24(3)	64.9(5)
APS	10.7(4)	5	5.2(2)	22(3)	61.5(3)
SCA989	10.5(3)	3	4.8(3)	23(4)	59.9(3)
MPS	10.3(4)	1	4.7(9)	21(3)	61.1(5)
Si ₃ N ₄	10.1(9)	-1	4.8(4)	22(6)	60.4(6)
SCA98	10.1(3)	-1	5.1(4)	17(2)	59.3(4)
VMS	10.1(2)	-1	4.7(4)	16(2)	59.3(3)
SCA984	9.9(3)	-3	5.1(3)	11(1)	57.7(5)

Table 5. Mechanical analysis of Silc composites.