Functionalised Silicon Nitride Fibres as Reinforcement in Epoxy Polymer Composites with Enhanced Mechanical Properties

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ABSTRACT

In this work silicon nitride (Si₃N₄) fibres were successfully functionalised with y-glycidoxypropyl trimethoxysilane (GPS) coupling agent. The surface modification was used as a method to enhance the dispersion and adhesion of the fibres in epoxy polymer composites. It is well known that strong interfacial adhesion between dispersed inorganic fibres and a polymer matrix improves the mechanical properties of the composite by providing an effective stress-transfer pathway between the matrix and the fibres. The functionalised Si₃N₄ fibres were dispersed into a commercial epoxy resin via tumble-mill mixing and ultrasonication. Setting was initiated via addition of a poly-amine hardener and the composites were cured at room temperature for 24 hours. The fractured surfaces of the cured composite materials were analysed via SEM imaging and the mechanical properties of the composites were tested. The GPS-Si₃N₄ composites were shown to have improved mechanical properties compared to the unfunctionalised Si₃N₄ composites, with improved tensile strengths and hardness values.

Keywords: polymer composites, interfacial adhesion, silicon nitride

1 INTRODUCTION

Epoxy resins are thermosetting polymers which crosslink on addition of a co-reactant or 'hardener', such as a polyfunctional amine. Cured epoxy polymers often have favourable mechanical properties, as well as good temperature and chemical resistance. This makes them useful for applications such as in adhesives, industrial coatings, electrical insulators and in fibre reinforced plastics.

Integration of filler particles or fibres can add value to the polymer material by combining their properties with that of the resin to produce a superior composite material. Polymer composites can be tailored for a specific application by adapting the surface chemistry, concentration or size of the filler materials. Silicon nitride (Si_3N_4) fibres are well suited to be an inorganic filler material in a polymer composite due to their favourable properties such as low thermal expansion coefficient, high aspect ratio, high tensile strength and good corrosion and thermal shock resistance [1–3].

Wang et Al [4] recorded the mechanical property improvements from adding unfunctionalised Si₃N₄ to

polyether ether ketone (PEEK). It was found that while hardness values increased linearly with increasing Si₃N₄ content, the bending and compressive strengths of the composite material were at a maximum at 1.25 wt% Si₃N₄. Xu et Al [5] studied the effect of incorporating silane functionalised nano-Si₃N₄ into polypropylene. They discovered that addition of 2 wt% functionalised Si₃N₄ increased the impact strength of the composite by 25 % and reduced the tensile strength by 10 %. They attributed this to an interruption in the polymerisation of PP resulting in a change in the crystal phase. There has also been research conducted on addition of Si₃N₄ fibres to polystyrene [6], polyethylene [7] and PMMA [3] showing it can be used to improve the mechanical, electrical and thermal properties of polymer composite materials.

Effective property transfer between the filler material and the matrix requires strong interfacial interactions and/or chemical binding between the two phases. Si₃N₄ fibres have a hydrophilic surface and a weak affinity to the hydrophobic epoxy polymer matrix causing poor interfacial adhesion and limiting the composite properties. Surface modification can therefore be used to enhance adhesion by chemically binding the fibres to the polymer matrix. Silane coupling agents contain various functional groups which allow the molecule to bond with both inorganic and organic materials. This makes them very useful for enhancing the adhesion of inorganic fibres to a polymer matrix and hence improving the mechanical properties of the composite material. In this paper, γ -glycidoxypropyl trimethoxysilane (GPS) is used as a coupling agent to form a chemical bond between the epoxy matrix and the dispersed Si₃N₄ fibres.

2 EXPERIMENTAL

Silicon nitride fibres (>95 % α - Si₃N₄) used for this study were provided by Nuenz Limited (New Zealand) and had lengths of 8 – 24 μ m and widths of 0.3 μ m. GPS coupling agent was provided by Struktol Company of America. The epoxy resin was a commercial West System 105 and the polyamine co-reactant was West System 206 slow hardener.

Hydroxylation of the Si_3N_4 fibres was used as a method to activate the surface and facilitate binding to the silane coupling agent. The fibres were dispersed in distilled water, sonicated and then heated to 60 °C and maintained, whilst stirred, for 18 hours. After cooling, the fibres were then separated from the liquid by centrifugation and dried in a vacuum oven at 60 °C for 24 hours.

To functionalise the activated fibre surface, a solvent solution of ethanol and water (95:5) was made up and its pH was raised to 8.5 - 9.0 via dropwise addition of sodium hydroxide. GPS coupling agent was added to the solvent solution to yield a 2 % concentration and stirred for 15 minutes to facilitate hydrolysis of the coupling agent. The hydroxylated Si₃N₄ fibres were then added to the solution and stirred for 10 minutes. The suspension was separated via centrifugation and rinsed twice with ethanol. The surface-modified fibres were dried in a vacuum oven at 60 °C for 24 hours or until completely dry.

The composites in this study were made at 1.0 vol% fibres in an epoxy polymer matrix (5:1 ratio of epoxy to amine hardener). The fibres were added to the epoxy resin and dispersed via tumble-mill mixing for 6 hours. The mixture was then degassed via sonication for 10 minutes and left to stand for 30 minutes. The amine hardener was added to the epoxy – fibre mixture and was thoroughly mixed to ensure uniform polymerisation. The mixture was then transferred into moulds and left for over 24 hours at room temperature to fully cure.

LECO TruSpec micro-CHN analysis was used to quantify the amount of carbon released from the fibre surfaces when heated to 950 °C using CaCO₃ as a standard. Thermogravimetric analysis (TGA) experiments were carried out on the fibres using a TA Q600 thermogravimetric analyser over a temperature range of 25 - 900 °C at a heating rate of 10 °C min⁻¹.

FT-IR analysis of the composite materials was carried out via ATR-IR on a Bruker Tensor 27 FT-IR spectrometer between 4000 and 500 cm⁻¹. 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.

Hardness measurements were taken using an industrial shore durometer (scale D) as per ASTM D2240 standard. Shore hardness values were compared to hardness compression tests using an Instron 3367 with a 10 mm diameter indenter ball at a loading rate of 2 mm min⁻¹ to a depth of 1.5 mm. Hardness values were taken as the slope of compressive load vs. compressive extension. Tensile tests were carried out using an Instron 3367 at a strain rate of 1.5 mm min⁻¹, using dog bone shaped samples according to ASTM D3039 standard.

3 RESULTS AND DISCUSSION

3.1 GPS Functionalisation of Si₃N₄ Fibres

CHN analysis was used to determine whether the GPS coupling agent was successfully bound to the fibre surface and to quantify the coverage.

	wt% Carbon	% Increase
Si ₃ N ₄	1.58 ± 0.02	-
GPS-Si ₃ N ₄	2.05 ± 0.02	0.47

Table 1: LECO CHN Analysis of GPS-Si₃N₄ Fibres.

Surface bound GPS contains 41 % carbon, therefore a 0.47 % measured increase in carbon for GPS-Si₃N₄ correlates to 1.15 wt% (0.47 % \div 0.41) of the material being due to the surface coverage of GPS on the Si₃N₄ fibres.

Brunauer-Emmet-Teller (BET) adsorption isotherms conducted on Si_3N_4 fibres estimated the surface area of the fibres to be 4.04 m²g⁻¹. The coverage area of GPS is known in the literature to be 330 m²g⁻¹.

$$\frac{Mass of}{GPS (g)} = \frac{Mass of Si_3N_4 (g) \times Surface Area of Si_3N_4 (m^2g^{-1})}{Coverage of GPS (m^2g^{-1})}$$
(1)

Calculations involving equation (1) predicted that 1.22 wt% surface coverage of GPS is required for a saturated mono-layer on a Si_3N_4 fibre surface. This value strongly agrees with the experimental value of 1.15 wt%.

TGA was also used as a method to quantify the coverage of GPS on the Si_3N_4 fibre surface (Figure 1). The TGA curves measured a total mass loss of 1.9 wt% for GPS- Si_3N_4 which approximately agrees with the previously measured value of 1.15 wt% from CHN analysis indicating a monolayer coverage.



Figure 1: TGA spectra of Si₃N₄ and GPS-Si₃N₄ fibres.

3.2 GPS-Si₃N₄ Epoxy Composite Analysis

The fibres were weighed and dispersed in the commercial epoxy resin, then cured with a polyamine to form the composite material at 1 vol% fibre ratio. The composites were analysed to determine whether GPS functionalisation had successfully enhanced interfacial adhesion between the fibres and the resin.

FT-IR analysis of the composites was conducted to observe whether the addition of GPS coupling agent affected the structure and bonding in the epoxy composite (Figure 2).



Figure 2: FT-IR spectra of GPS-Si₃N₄, Si₃N₄ and neat epoxy polymer composites.

The broad absorption peak at 3380 cm⁻¹ in the epoxy polymer spectrum (Figure 2 (3)) was due to C-OH stretches overlaid with NH₂ and N-H stretching frequencies. These functionalities are formed when the amine groups in the hardener react with the epoxy groups in the resin. Addition of GPS-Si₃N₄ to the resin causes a lowering in the wavenumber of this adsorption to 3363 cm⁻¹ and a broadening of the peak. This is due to the epoxy groups on the silane coupling agent binding to the amines and causing a reduction in the vibration frequencies. This peak shift provides evidence for a chemical interaction taking place between the coupling agent and the resin matrix.

SEM analysis was carried out on the fracture surfaces of the composite materials. The micrographs confirmed there was homogeneous distribution of Si_3N_4 fibres within the polymer composite matrix and there was no visual evidence of agglomeration in the samples.

SEM micrographs of Si_3N_4 epoxy composites displayed an interfacial gap at the fibre – polymer boundary (Figure 3). The Si_3N_4 fibres are seen to be loosely placed within the epoxy matrix, indicative of weak interfacial adhesion and poor wetting of the fibres by the resin.



Figure 3: SEM micrograph of the fracture surface of Si_3N_4 epoxy composites at x17,000 magnification.

Interfacial gaps or voids greatly reduce the transfer of applied stresses from the matrix to the fibres and therefore reduce the mechanical strength of the composite material.

The fracture surfaces of Si_3N_4 composites showed multiple locations where the fibres had been pulled out of the matrix during the fracturing process (Figure 4). 'Fibre pullout' is the principal failure mechanism in fibre – polymer composites and is indicative of weak interfacial adhesion.



Figure 4: SEM micrograph of 'fibre pull-out' in Si_3N_4 epoxy composites at x6,000 magnification.

SEM images of GPS-Si₃N₄ epoxy composites (Figure 5) confirmed there was improved interfacial adhesion between the GPS-Si₃N₄ fibres and the polymer matrix. A 250 nm thick organic coating, composed of GPS bound to a layer of epoxy resin, encased the fibres. Efficient wetting of the fibres prevented the formation of interfacial voids and there was no evidence of 'fibre pull-out' at the fracture surfaces.



Figure 5: SEM micrograph of GPS-Si₃N₄ epoxy composite fracture surface at x17,000 magnification. Organic coating consists of epoxy resin bound to the fibre surface by GPS.

A clear majority of the fibres located along the fracture surface in GPS-Si₃N₄ composite had successfully adsorbed the applied stresses on the material and had fractured along the same interface as the epoxy matrix. This illustrates the strong interfacial adhesion between the fibres and the resin, and the successful transfer of properties across the interface.



Figure 6: SEM micrograph of the fracture surface of GPS-Si₃N₄ epoxy composites at x17,000 magnification.

The SEM micrographs provided visual evidence for the enhanced adhesion and bonding between the GPS functionalised fibres and the epoxy resin matrix when compared to the as-received fibres.

3.3 Mechanical Testing

The hardness values of the polymer composite samples were tested via an industrial standard, shore hardness (scale D). The results were compared to calculated hardness values (in kgf mm⁻¹) obtained from the slope of compressive load (kgf) vs. compressive extension (mm) graphs recorded during an indentation test on an Instron.

Composite	Shore Hardness	Hardness* / kgf mm ⁻¹ (% increase)
Epoxy	80.4 ± 0.4	472 ± 9
1 % Si ₃ N ₄ Epoxy	82.5 ± 0.3	506 ± 24 (7 %)
1 % GPS-Si ₃ N ₄ Epoxy	84.5 ± 0.3	532 ± 4 (13 %)

Table 2: Shore hardness values and calculated hardness values for epoxy polymer composites. *Slope of compressive load vs. compressive extension.

The hardness values measured via the two techniques both displayed a clear trend that 1 vol% GPS-Si₃N₄ fibres improved the hardness values of an epoxy composite material to a far greater extent than Si₃N₄ fibres alone. These results demonstrated the increased property transfer achieved from efficient adhesion.

The ultimate tensile strength (UTS) was measured for the different composite materials using an Instron tensile tester.

Composite	UTS (MPa)	% Increase
Epoxy	37.5 ± 1.9	-
1 % Si ₃ N ₄ Epoxy	39.5 ± 2.9	5 %
1 % GPS-Si ₃ N ₄ Epoxy	47.6 ± 5.7	27 %

Table 3: Tensile test results for epoxy polymer composites.

The results showed a similar trend to the hardness values and measured a small improvement in tensile strength on addition of 1 vol% Si_3N_4 fibres and a significant improvement on addition of 1 vol% GPS- Si_3N_4 fibres in the epoxy resin.

4 CONCLUSION

Interfacial adhesion in polymer composites is a key contributor towards achieving superior composite performance and improved mechanical properties. In this work surface functionalisation techniques were used on Si_3N_4 fibres to improve their adhesion in an epoxy matrix and achieve enhanced mechanical properties.

 Si_3N_4 fibres were successfully functionalised with a mono-layer coverage of GPS coupling agent. FT-IR analysis provided evidence that GPS was chemically interacting with the polymer matrix. The surface functionalisation created a strong chemical link between the fibres and polymer matrix, allowing for efficient transfer of properties. SEM images of the fracture surfaces confirmed improved adhesion and comparisons between the failure mechanisms in Si_3N_4 and GPS- Si_3N_4 composites demonstrated enhanced interfacial interactions between the GPS functionalised fibres and the resin.

Mechanical testing (hardness and tensile tests) confirmed that improved adhesion in GPS-Si $_3N_4$ composites led to an increase in the mechanical performance of the composite material.

AKNOWLEDGEMENTS

The authors would like to thank Callaghan Innovation and Nuenz Limited for providing the funding to complete this research project, Victoria University of Wellington and the Product Accelerator - University of Auckland for providing testing facilities and Struktol Company of America for providing silane coupling agents.

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