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SILANE MODIFICATION OF THE FLAX/EPOXY SYSTEM INTERFACE

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Abstract

Natural fibres (NF) are normally subjected to pre-treatment to ensure good fibre to matrix bonding and consequent mechanical properties and durability. To enhance the sustainability of NF composite systems, it would be sensible to minimise processes that incur environmental burdens. This research considers that addition of silane coupling agent to epoxy resin hardener may be an alternative to the direct chemical pre-treatment of NF before composites manufacture. The current study indicates that silane-in-hardener can eliminate the pre-treatment of fibres and generates composites with optimum mechanical properties.

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1. Introduction

Good mechanical (stiffness and strength) performance in a composite system is normally achieved when the fibres are well-bonded to the matrix. In glass fibre reinforced unsaturated polyester resin, the fibres are coated with a coupling agent where the molecule has a silane group to bond to the fibre and a vinyl group to react with the unsaturation in the resin. The coupling agent will often have an oleophilic/hydrophobic end in the resin and an oleophobic/hydrophilic end at the fibre matrix interface.

1.1. Silanisation of natural fibres

For natural fibre composites, chemical treatment of the fibres with silanes (silanisation) is often used to enhance the fibre/matrix interfacial bonding. Xie et al. [1] have reviewed direct silanisation of natural fibres (broadly flax, sisal and hemp). The creation of covalent bonds over the whole fibre surface occurs by reaction between hydroxyl (OH) groups on the fibre surface and those in the silane molecule (Fig.1). This reaction should lead to natural fibre composites with improved mechanical properties and durability.
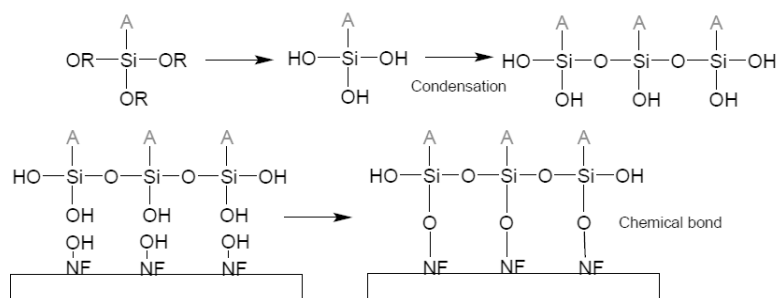

Fig. 1. Si-O-Si bonding scheme

Van de Weyenberg [2] studied different fibre pre-treatments for flax fibre. All the methods started with mercerisation (1, 2 or 3% NaOH solution for 20 min at RT) of the fibres. The fibres were then thoroughly washed in cold water, then acidified water (20 drops of 0.1 M HCl/litre of water) to neutralise the NaOH. The fibres were again rinsed in cold water, then dried in an oven at 80°C for 8 h. The silanisation involved soaking fibres in a 1% solution of 3-aminopropyl trimethoxy silane in equal volumes of acetone and water for 2 h. The fibres were again dried in an oven at 80 °C for 8 h. The longitudinal modulus and strength were increased by ~58% and ~38% when the fibre was treated with 1% NaOH solution then 3% epoxy resin solution. The longitudinal modulus and strength were increased by 46% and 4% respectively after treatment with 1% silane. The transverse modulus and strength were increased by 400% and 110% respectively after silane treatment.

Xie et al. [1] reviewed the use of silane coupling agents (generally trialkoxysilanes) in NF/polymer composites to improve the interfacial properties. The generic chemical structure of the silane coupling agents is $A_{(4-n)}$-Si-$(R'X)_n$ (n = 1,2) where A is alkoxy (alkyl ether), X represents an organofunctional group, and R' is an alkyl bridge. The alkoxy normally reacts with the NF surface and the R' organofunctional group is compatible with the organic polymer matrix due to their similar polarities. The organofunctional entities in the silane may be amino-, mercapto-, glycidoxy-, vinyl-, or methacryloxy- groups. Aminosilanes, especially γ-aminopropyltriethoxysilane (APS), are most commonly reported coupling agents used for natural fibres in polymer matrices.

Gliesche and Mäder [3] used silane (OSi-Specialties A-1100 or A-1120) coupling agents for flax and ramie fibres. Typical water contact angles for the untreated flax and ramie fibres were 87° and 77° respectively.

The silane treatment of the cellulose fibre surface may produce polymer grafting and decrease hydrophilicity. Abdelmouleh [4] treated fibres with 5 w/o silane in stirred 80/20 v/v ethanol/water mixture for 2 h, dried the fibres at RT for days, then cured the system under nitrogen atmosphere at 120°C for 2 h. O-Si-O and C-Si-C bridges were reported to have formed between the fibre surface and silane groups. Shokooi [5] reported that Si–O–C bonds in natural fibre composites are less stable under hydrolysis than the Si–O–Si bonds in glass fibre composites.

Hassan et al. [6] reported improved tensile strength, elongation to break and durability for mercerised jute fibres grafted with silanes and acrylamide under ultraviolet radiation.

Kabir et al. [7] subjected hemp fibres to alkali, acetyl and silane treatments. Hemp fibre directly treated with silane showed drastically reductions in mechanical properties: -61% and -33% for tensile modulus and strength respectively. For silane applied to previously mercerised fibre, the properties were enhanced, although they did not reach untreated fibre composite mechanical properties.

Zhou et al. [8] reported that silane-treated sisal fibres formed covalent bonds. Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) indicated that the silane treatment changed the surface topography and chemical structure, and lead to thermal degradation of the sisal fibres.

Guduri et al. [9] reported toughening of Hildegardia NF reinforced epoxy matrix with polycarbonate polymer. For NF treated with NaOH solution for 1 h then sprayed with 1% silane coupling agent over the surface, the adhesion between fibre and matrix increased, but the water resistance fell. This may be because the fibre surface becomes more polar, and consequently the hydrophilicity increases.

Liu et al. [10] proposed a combined chemical treatment for the improvement of transverse mechanical properties of unidirectional (UD) abaca fibre/epoxy system. The six-part method was (i) RT mercerisation of the fibre in 1.0 w/o NaOH solution for five minutes or in 5.0 w/o NaOH solution for 30 minutes, (ii) thorough washing with water, (iii) dried at 70°C, (iv) silane treatment of the mercerised fibre in (1.0 w/o γ-glycidoxypropyl-trimethoxy silane, 1.0 w/o acetic acid, 49 w/o alcohol and 49 w/o water prepared mixing all the components in an opaque container for 60 minutes) solution for 24 h and constant 5.3 pH, (v) washed with distilled water and kept at RT for 30 minutes and finally (vi) dried in the oven at 100°C for 2h. They concluded that covalent bonding between the fibres and silanes increased the interfacial adhesion and thus improved the mechanical properties and durability of the resulting composites. For abaca fibre composites ($V_f = 0.3$) mercerised with 5% NaOH for 30 min before silanisation, the composite transverse tensile strength increased by 80%.

Rong et al. [11] reported that silanisation for a sisal/epoxy system saw tensile modulus and strength decrease, while there was a 47% increase in strain at break. Zahari [12] produced silanised ijuk/PP composite with tensile strength was increased by 17% but little improvement seen for the water absorption properties. Asumani et al. [13] reported a 50% increase in tensile modulus for kenaf/PP/silane composite.

Cantero et al. [14] studied different chemical treatments in the flax/PP composite system. Flax fibre treated with vinyl trimethoxy silane had a 9% increase in tensile modulus and 5% decrease in tensile strength. The flexural properties were negatively affected by the silanisation.

1.2. Silane-in-the-matrix for synthetic fibre composites

An alternative route to enhanced fibre matrix bonding in synthetic fibre, e.g. carbon fibre (CF)/epoxy, composites is addition of the silane coupling agent to the matrix, rather than surface treatment of the fibres. Georgiopoulos et al. [15] studied three different biodegradable matrixes treated with silane, but found no real improvement in the composite mechanical properties.

Bogoeva-Gaceva et al. [16] studied the factors affecting the CF/epoxy interface. Surface chemical groups were identified to evaluate their effect on the epoxy resin curing process. Conventional interface evaluation methods, such as fibre pull-out tests, with thermal DSC and TGA techniques indicated that oxidation of the CF surface provides a definite enhancement in fibre/epoxy adhesion.

Since good wetting of a substrate is important for the achievement of a good interface, many studies have been performed to investigate wetting methods for CF fibre. Xu [17] wrote that the utilisation of acrylic acid in the epoxy resin formulation substantially increases the wettability of the fibre tows, directly improving the interface properties.

Chen et al. [18] evaluated a new T800 CF sizing for the increment of the interface with resin reformulated for enhanced toughness and increased fibre wetting. Both factors directly increased the interface properties. The matrix toughness enhanced the interface, while improved wetting created mechanical anchoring between the rough CF surface and the matrix. The NOL (Naval Ordnance Laboratory)-ring shear test method, may indicate doubling of interface/interphase bonding when both the fibre sizing and resin reformulation effects are considered.

The aim of any epoxy resin reformulation is to achieve a determined performance and to increase the adhesion with the fibre. Wang [19] and Chruściel [20] introduced silanes, siloxanes or silsequioxanes into the epoxy resin backbone to enable covalent chemical bonds between the resin and fibre and hence increase composite performance.

Brantseva et al. [21, 22 and 23] reported the importance of reducing the resin surface energy for the better wetting of the glass fibres (GF). They reported that when epoxy resin was modified with 10 w/o polysulfone, the composite interfacial properties were increased.

Onjun [24] reported that silane in an epoxy matrix migrated to the interfaces where it creates a bridge between glass fibre and matrix and hence enhances the composite long term mechanical performance and the hygrothermal resistance due to an increase in the composite subcritical debonding energy (G).

Although the literature has many references to direct silanisation of natural fibres, the authors are not aware of any previous reference to the addition of silanes to the matrix for natural fibre composites. This paper considers the possibility of using silanes in the matrix to reduce/eliminate fibre pre-treatment while also achieving optimum composite properties. It is anticipated that the incompatibility of the organofunctional group with the resin will result in that entity being driven to any surfaces or interfaces in the system where it may react with other species present, especially the natural fibre surface.

2. Materials

2.1. Flax fibre

Composites Evolution (CE/Chesterfield - England) produces flax and/or jute yarns and fabrics under the trade name Biotex [25]. This study used CE unidirectional (0° UD) 275 gsm flax fabric. The CE fibre properties are shown in Table 1.

Table 1. An example of a table.

Flax fibre average properties	
Density	1500 kg/m^3
Diameter*	20 μm
Tensile modulus	50 GPa
Tensile strength	500 MPa
Strain at failure	2%

* An "apparent" diameter was estimated: natural fibres normally have a non-circular cross-section.

2.2. Epoxy resin

In this study, composite production used Araldite LY 1569 CH/Aradur 3489 CH petrochemical-based epoxy infusion resin from Huntsman LLC. (USA) [26].

2.3. Chemical products

Sodium hydroxide (NaOH; CAS #1310-73-2; molecular weight 40; granules) was sourced from Sigma-Aldrich [27]. Ethanol (C_2H_5OH; CAS #64-17-5; molecular weight 46.07; thin clear liquid) was sourced from Sigma-Aldrich [28]. The silane coupling agent for epoxy composites was 3-(trimethoxysilyl) propylamine ($C_6H_{17}NO_3Si$; BYK-C 8001; CAS #82985-35-1; molecular weight 179.29; viscous liquid) [29] (Fig. 2).
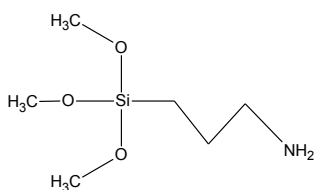

Fig. 2. 3-(trimethoxysilyl) propylamine structure

3. Experimental

The fibres were assumed to be supplied untreated and were subjected to four different treatments as described in §3.1.

3.1. Treatments

3.1.1. Biotex flax/Huntsman epoxy + 1.5% silane in hardener

Laminate 1 was manufactured with untreated Biotex flax reinforcement. The Huntsman epoxy system (Araldite LY 1569 CH/Aradur 3489 CH) was supplemented with 1.5% silane initially added to the hardener.

3.1.2. Biotex flax/Huntsman epoxy + mercerised + 1.5% silane in hardener

Laminate 2 was manufactured with Biotex flax fibre mercerised for 3h at 1M NaOH concentration (determined to be the best fibre treatment in an earlier study/not published). As for laminate 1, 1.5% silane initially added to the hardener for the Huntsman epoxy resin system.

3.1.3. Biotex flax/Huntsman epoxy + 1% silane treated fibre

Laminate 3 was manufactured with unmercerised Biotex flax fibre which had been treated with 1% silane solution (50/50 v/v ethanol/water) for 1h at RT, then dried at RT for 48h. The standard Huntsman epoxy system (Araldite LY 1569 CH/Aradur 3489 CH) was used without addition of silane.

3.1.4. Biotex flax/Huntsman epoxy + mercerised + 1% silane treated fibre

Laminate 4 was manufactured with Biotex flax fibre which had been mercerised for 3h at 1M NaOH concentration, treated with 1% silane solution (50/50 v/v ethanol/water) for 1 h at RT, then dried at RT for 48h. The standard Huntsman epoxy system (Araldite LY 1569 CH/Aradur 3489 CH) was used without addition of silane.

3.2. Panel infusion

The four laminates manufactured by resin infusion under flexible tooling with a flow medium (RIFT II) following the scheme illustrated in Fig. 3. Laminates were manufactured on an AMOND lamination table controlled with its own software, then cured at ambient temperature in an electrically heated mould tool.
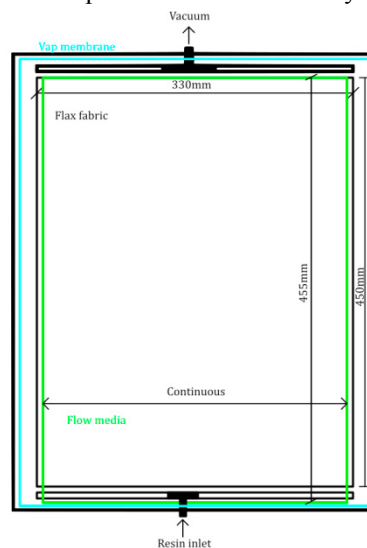

Fig. 3. Laminate 1-4 lamination scheme

3.3. Sample cutting

Mechanical test samples were prepared using a Mutronic DIADISC 5200R cutting machine. The use of a diamond saw blade caused burning of the flax/epoxy composite panel surfaces. While the cut was precise and clean, the friction produced by the saw caused ignition of the generated dust. A substitute hard steel saw blade (higher thermal conductivity) produced precise clean cuts, without burning the samples.

3.4. Tab gluing

Tabs were manufactured using two layers of biaxial 1200 gsm glass fibre fabric then adhered to the sample ends with Araldite 2015 bi-component epoxy adhesive [30] to avoid the premature failure in the grip area. The adhesive was cured at RT for 1h followed by an oven post-cure at 60ºC for 1h.

3.5. Testing

Mechanical testing was performed on a Shimadzu AG-X PLUS 250KN, computer coupled universal testing machine with a 100 kN load cell using Trapezium X software and accuracy class 0.5 according to UNE-EN-ISO-7500-1:2006.

3.6. Standards

Tensile tests were conducted in accordance with the ISO 527-4/-5 standards. The different characteristics for the longitudinal and transverse tests are summarised in Table 2.

Table 2. Longitudinal tensile test conditions

	ISO 527-4/-5 longitudinal tensile test conditions	ISO 527-4/-5 transverse tensile test conditions
Number of specimens	10	10
Specimen dimensions	250mm x 15mm x a (mm)	250mm x 25mm x a (mm)
Tabs type	Double bonded ±45° GF/epoxy	Double bonded 45°GF/epoxy
Tabs dimensions	50mm x 15mm x a (mm)	50mm x 25mm x a (mm)
Free length between tabs	150mm	150mm
Test speed	2mm/min	2mm/min
Strain measurement	Video extensometers	Video extensometers
Test climate	ISO291 class 2	ISO291 class 2

4. Results

The study was performed on four different laminates:
1. Unmercerised unsilanised flax/epoxy with 1.5% silane-in-hardener,
2. Unmercerised silanised flax/epoxy with 1.5% silane-in-hardener,
3. Unmercerised silanised flax/epoxy with no silane in the resin,
4. Mercerised silanised flax/epoxy with no silane in the resin.

Table 3 presents the longitudinal and transverse test results measured for the four systems tested according to the ISO527-4/5 standard: E_1, S_1 and ε_1 values were obtained from the longitudinal tests, while E_2, S_2 and ε_2 values were obtained from the transverse tests.

Table 3. Mechanical properties

	1-Biotex/Huntsman SiHard	2-Biotex/Huntsman NaOH (1M 3h) +SiHard	3-Biotex/Huntsman SiFib	4-Biotex/Huntsman NaOH (1M 3h) +SiFib
E_1	13.08	10.08	10.05	10.88
E_2	3.66	4.08	3.72	3.87
S_1	136.46	105.24	120.50	95.49
S_2	16.65	14.11	17.53	19.28
ε_1	1.29	1.92	1.57	1.44
ε_2	0.36	0.33	0.44	0.50

5. Conclusions

The data in Table 3 suggests that the optimum mechanical properties (highest longitudinal modulus and strength) are achieved when silane is added to the epoxy resin hardener before laminate manufacture and the fibres are used in their raw state. The use of raw state fibres reduces the environmental burdens arising from chemical treatments (NaOH and polluted waste solvents) and from the energy required for drying the treated fibres. Further, mixing silane with hardener rather than chemical treatment of the fibres, can save considerable time in the natural fibre composite production system.

Acknowledgments

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