The Effect of Sodium Ions on the Stability of the Interphase Region of Glass Fibre Reinforced Composites

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The single embedded filament fragmentation and the short beam shear strength tests together with angle-resolved X-ray Photoelectron Spectroscopy (XPS) have been used to investigate the interfacial region of vinyl ester composites reinforced with sized AR-glass fibres, with and without amino and vinyl functional adhesion promoters.

The γ-aminopropyltriethoxysilane (APS) deposit on AR-glass is susceptible to a thermal degradation during post-cure, which has been attributed to a base catalysed equilibration of the siloxane bonds. The functional groups of APS required for resin compatibility were buried beneath the surface layers, contributing to a low bond strength, furthermore, mobile sodium ions existed within the interfacial region. Aqueous extraction prior to fabrication enhanced the composite bond strength by removing the soluble silane oligomers, the sodium ions, and exposing the organo-functional groups for co-reaction with the matrix.

The silane deposit on AR-glass is made hygroscopic by the presence of sodium ions. This increased the equilibrium moisture content of AR-glass composites, and diminished their retained short beam shear strength in contrast to the E-glass control which retained its properties after redrying.

KEY WORDS Silane; adhesion promoter; composite; vinyl ester; AR-glass; X-ray photoelectron (XPS); Lewis acids and bases; embedded filament fragmentation; interlaminar shear strength.

INTRODUCTION

Glass fibres form the basis of industrial composites, finding application in low volume production mouldings, short fibre reinforced components and high performance applications. Immediately after the spinning process, glass fibres are given a surfacce treatment usually in the form of a size or a finish, which has several functions; to displace the adsorbed water, to create a surface which can be fully wetted by the resin matrix, to develop strong interfacial bonds and to produce a handleable product. These contain several additives, which include one or more

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adhesion promoters called silane coupling agents, a lubricant, and a film-forming polymer. The adhesion promoter contains three alkoxide groups and an organo-functional group; the former readily hydrolyse to silanol groups, for condensation with silanol groups on the glass surface, with the formation of a covalent bond. This reaction is considered by Plueddemann[1] to be reversible, allowing for the accommodation of shear at the interface. The fourth group is chosen to react with the polymeric resin during processing, to achieve a "coupling" between the fibre and matrix. Several models for the interfacial region have been described;[1] however, they all have their limitations. The formation of an interfacial bond between the functional groups of the resin and the matrix is the one generally accepted.

Silane coupling agents deposited onto glass substrates have a multilayered structure of differing hydrolytic stability, so that a polysiloxane interphase is created between the matrix and the reinforcement.[2] Thick layers of the silane deposit can be deleterious to the performance of composites;[3] however, to date the influence of these regions on the bond strength of composites has not been conclusively demonstrated.

The embedded single filament tensile test was adopted to investigate this phenomenon for different silane-treated fibres. By aqueously conditioning the fibres to extract the layers of varying hydrolytic stability from the fibre surface, prior to composite fabrication, the influence of these on the bond strength could be established. Confirmation of these observations was provided by measuring the interlaminar shear strength (ILSS) of equivalent unidirectional composites using the short beam shear strength test.

Most of the benefits of the adhesion promoter are realised under humid environments through improved durability. In this paper, we have used differences in ILSS to study the role of two silanes, one of which has an oligomeric physisorbed component, APS, and the other a highly crosslinked, but more compatible coating, vinyl triethoxymethoxysilane (VTS), on the interfacial stability of AR-glass fibre, vinyl ester composites.

The nature of the silane deposit has been studied in depth using Fourier Transform Infrared (FT-IR) Spectroscopy, XPS and time-of-flight secondary ion mass spectroscopy (ToF SIMS).[2,4,5] Wang and Jones[4] used XPS to study the interaction of hydrolysed APS (HAPS) with a flat E-glass slide surface. They demonstrated that a HAPS coating of approximately 6 nm is deposited, which consists of three components of differing molecular structure. The outer surface comprised a warm-water soluble oligomer in which the amino group is in a non-hydrogen bonded form. Beneath, a 3-D graded network exists whose ends, after extraction with water, were believed to be involved in an internally hydrogen-bonded structure between the amino and silanol groups, probably in a cyclised conformation. Adjacent to the glass surface, a molecular layer of HAPS remained after extraction with hot water, which was chemically bound to the glass surface through siloxane and/or aluminoxane bonds.

In previous papers[6-8] we have reported the preliminary results of a study of AR-glass fibres in a vinyl ester matrix. In this paper, XPS has been used to complement a mechanical testing programme to provide an insight into the performance of vinyl ester composites reinforced with alkali/acid resistant AR-glass fibres.

EXPERIMENTAL

Materials

The vinyl ester resin, Derakane 411–45 (Dow Chemical Co), was cured using 2 phr (parts per hundred) of a 50% methyl ethyl ketone peroxide solution (catalyst M), 1 phr of a cobalt naphthenate solution (Accelerator E, Scott Bader and Co) and 0.5 phr of dimethyl aniline (10% in styrene). AR-glass fibres (Pilkington Reinforcements Ltd) were supplied with a common size but differing silanes; one contained γ-aminopropyltriethoxysilane (APS) (A1100; Union Carbide, now OSi Specialities Inc), one the vinyltriethoxysilane (VTS) coupling agent (A172; Union Carbide) and the other no adhesion promoter (NAP). Commercial silanised E-glass fibres were supplied with an epoxy/polyester compatible size (SILENKA 084; PPG Holland).

Interfacial Shear Strength Measurements

The embedded monofilament tensile test was used to measure differences in the interfacial shear strength (τ). The data analysis employed the standard Kelly-Tyson method.[9] The reproducibility of the technique is such that direct comparison of individual values obtained using the same matrix system can yield significant conclusions.[5] In this analysis, we have used variational statistics to provide confidence limits to the values of τ as described elsewhere.[10]

Fibre tows were removed from the rovings at random, subjected to one of the treatments shown in Table I and dried in vacuo at 50°C. Then 65 mm × 10 mm × 2 mm test pieces were prepared with individual filaments using established techniques;[11] care was taken not to touch the central part of the fibres. The specimens were cured at room temperature for 24 hrs, then the thickness of the central portion

TABLE I

The effect of fibre conditioning on the interfacial shear strength τ (MPa) of cold-cured vinyl ester AR-glass composites

Fibre Treatment	APS		VTS		NAP		E	
	τ (MPa)	$\bar{\sigma}_{fu}$ (GPa)	τ (MPa)	$\bar{\sigma}_{fu}$ (GPa)	τ (MPa)	$\bar{\sigma}_{fu}$ (GPa)	τ (MPa)	$\bar{\sigma}_{fu}$ (GPa)
As-received	13.8 (2.2)	2.2 (0.3)	15.0 (3.1)	2.1 (0.4)	14.4 (3.2)	1.8 (0.4)	15.3 (4.0)	2.4 (0.6)
Warm-water extraction (50°C)	18.2 (3.0)	1.6 (0.25)	14.8 (3.2)	1.5 (0.3)	13.0 (3.3)	1.5 (0.3)	16.9 (4.2)	1.7 (0.4)
Hot-water extraction (100°C)	17.7 (6.2)	1.6 (0.5)	17.3 (5.1)	1.4 (0.4)	12.6 (3.1)	1.3 (0.3)		
Heat treated at 130°C for 1½ hrs	10.1 (2.8)	1.5 (0.4)	10.8 (3.6)	1.4 (0.4)	9.8 (2.9)	1.3 (0.4)	7.8 (2.1)	1.9 (0.5)

APS = γ-aminopropyltriethoxysilane. VTS = vinyltriethoxysilane. NAP = without silane.
E = epoxy/polyester compatible E-glass control. $\bar{\sigma}_{fu}$ = average fibre strength at 6.35 mm.

was milled down to 1 mm and the end portions to 1.5 mm. This reduced the risk of grip-initiated premature failure. A cerium oxide polishing wheel was used to produce a transparent finished product.

Prior to testing, each specimen was examined under an optical microscope to separate those containing defects which must be eliminated from fracture length analysis. Specimens which failed during testing were not examined further because the shock can induce additional failures.[12] The test pieces were pulled in uniaxial tension at 0.2 mm/min until the number of fractures within the filament became constant. The individual fragment lengths were measured with a calibrated optical microscope.

The critical length, L_c, required for the calculation of τ, was obtained from the average fragment length , L, according to the standard equation

$$L = 4L_c/3$$

τ was obtained by assuming that the Kelly-Tyson analysis[9] was applicable, which gives the following relationship:

$$\tau = \sigma_{fu} d/2L_c$$

where σ_{fu} is the fibre tensile strength at the critical length and d is the fibre diameter. The values of τ quoted in this work are calculated using the maximum likelihood method and Weibull statistics described in detail elsewhere.[10,13] This method takes into account the fragment length statistics and therefore the values of τ differ slightly from those reported elsewhere.[6-8]

Single Filament Strength Measurement

Fibre glass tows were removed from the rovings, and subjected to one of the treatments described in Table I. Monofilaments were selected at random from the treated glass tows and mounted on window cards using card end-tabs to secure them in place at an exact gauge length of 6.35 mm.[14,15] A specially constructed spring loaded grip clamped the top edge of the specimen and was attached with a hook to the load cell. This enabled the grip to rotate freely and ensured good alignment of the sample during testing. A load cell with a 50 g full-scale deflection and a displacement rate of 5 mm/minute was employed. The tests were carefully monitored to ensure that only data for tests which failed in tension were collected.

Interlaminar Shear Strength (ILSS) Determination

For the ILSS measurements, unidirectional specimens of regular square-sided blocks with the reinforcing fibres running parallel to the length were fabricated using conventional laminating techniques.[14,15] After curing for 24 hours at 20°C, test pieces of 20 mm × 8 mm × 4 mm were cut from the laminate using a water-cooled rotary diamond impregnated wheel. The specimens were cured and conditioned according to Tables II & III.

ILSS tests were performed on a Mayes SM 200 Universal Testing Machine using a three point bend rig with a span-to-depth ratio of 3.75:1, at a ram speed of 0.2 mm

per minute. The test pieces were located symmetrically on the support rollers and the loading roller was constrained to move vertically above the centre line of the test piece. A 2 kN load cell in conjunction with an extensometer created a load/displacement curve from which the maximum load at the point of failure was determined. Using these conditions, the majority of the samples failed in shear; those which did not were discarded. Negligible damage occurred at the contact point between the specimen and the loading noses whose radii of 3.2 mm was within the range recommended in the ASTM specifications.[16]

The ILSS was calculated according to the relationship,

$$ILSS = 0.75P/tw$$

where P is the load at which shear failure occurs and t and w are the specimen thickness and width, respectively.

Surface Analysis by X-ray Photoelectron Spectroscopy (XPS)

For XPS analysis, AR-glass cullet, used in the spinning process, was cast into plates and cut into slides of 8 mm × 8 mm × 2 mm using a diamond impregnated rotary cutting wheel. These were ground to 1 mm, polished to better than 1 μm using a diamond paste wheel, washed several times with deionised water, then heat cleaned at 200°C for 0.5 hrs. The slides were treated in a 1.5 wt% solution of APS in either deionised water or Analar methanol, at room temperature, then dried in vacuo at 50°C. A control, a polished plate, was heat treated at 200°C immediately prior to analysis.

To assess the effect of aqueous extraction and subsequent heat treatment at the post-curing temperature used in composite fabrication, the following series of experiments were conducted on freshly prepared glass slides which had been polished and washed with methanol and distilled water:

After silanisation, washing and drying in vacuo at 50°C overnight as above,

1. the sample was heat treated at 130°C for 1.5 hours,
2. immersed in distilled water at 50°C for 1 week and dried in vacuo at 50°C overnight,
3. after conditioning as in 2, it was heat treated at 130°C for 1.5 hours,
4. immersed in boiling water for 4 hours and dried in vacuo at 50°C,
5. after conditioning as in 4, it was heat treated at 130°C for 1.5 hours.

Both samples from treatments 3 and 5 were analysed immediately.

The first set of plates were mounted onto individual aluminium specimen holders, using double sided Sellotape, for analysis in a VG Scientific ESCA lab Mk 11, Spectrometer, operating under a vacuum of $< 10^{-9}$ torr, with Al($K\alpha$) radiation. The Spectrometer was interfaced to a VG 5000S data system, based on a PDP 11/73 computer. Each specimen was analysed by a combination of a 1100 eV survey and 20 eV high-resolution scans for all the relevant elements that should be present: carbon, oxygen, sodium, silicon, zirconium, calcium, aluminium and nitrogen. All the survey scans were conducted at a take-off angle of 45°. The narrow spectra of the

individual elements were obtained at 15°, 30° and 45° relative to the plate surface, to vary the analysis depth from approximately 3–5 nm. The second set of analyses were carried out on a VG Microtech Clam 100 XPS using Mg($K\alpha$) radiation at an operating power of 10 keV and 10 mA with a pass energy of 50 eV. Typical spectra from these experiments are given Figure 1. A discussion of the analysis depth has been presented in a previous publication by Wang and Jones.[4]
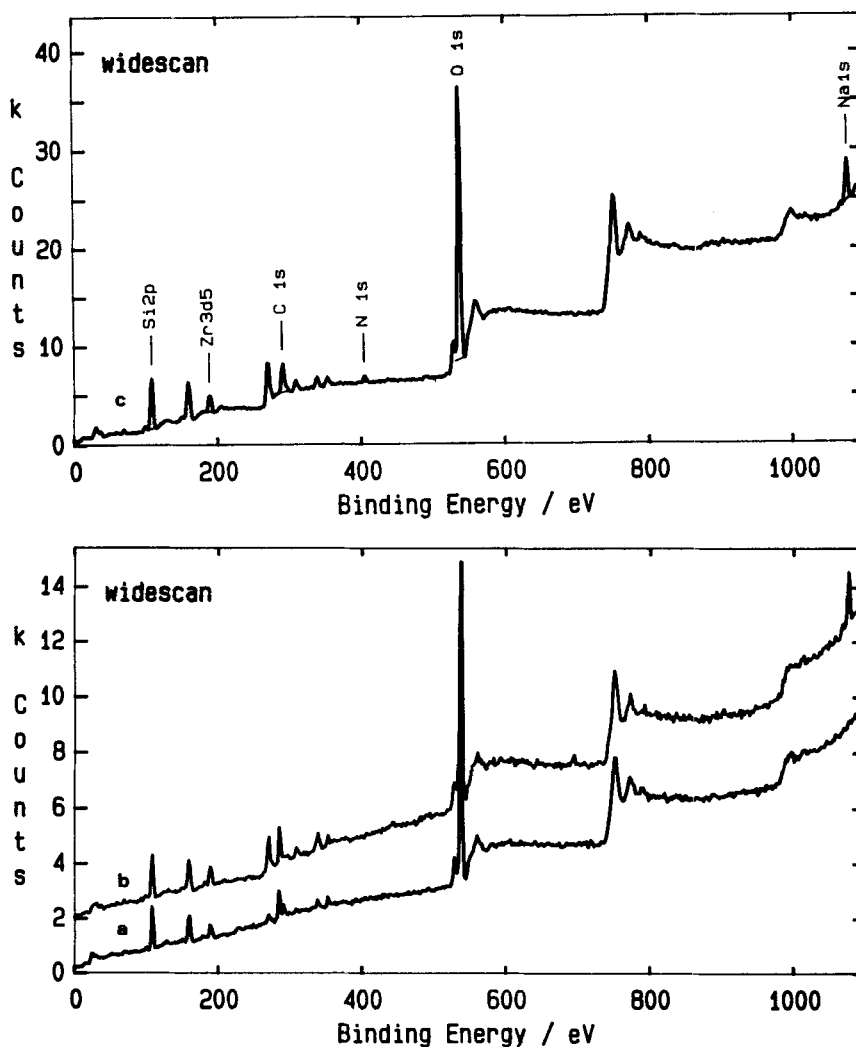

FIGURE 1   Effect of heat treatment on the XPS spectra of silanised AR-glass surfaces showing (a) polished glass control, (b) heated treated (200°C) (c) APS-silanised as-polished AR-glass surface after heat treatment at 130°C for 1.5 h.

Environmental Conditioning

Interfacial shear strength samples   Fibre tows were selected at random from each of the four types of glass fibre reels. From these the following different types of samples were prepared. .

1) As-received samples:
   Single filaments of each of the four types of glass fibre were carefully removed from the fibre tows at random.
2) Warm-water extraction:
   The four types of fibre tows were immersed in deionised water at 50°C for 28 days. From these, single filaments were carefully removed from the fibre tows at random.
3) Hot-water extraction:
   The four types of fibre tows were immersed in deionised water at 100°C for 28 days, then dried in vacuo at 50°C for 28 days. From these, single filaments were carefully removed from the fibre tows at random.
4) Heat treated fibres:
   The four types of fibre tows were placed in a pre-heated, air circulating oven at 130°C for 1.5 hrs, then cooled in the oven to room temperature. From these, single filaments were carefully removed from the fibre tows at random.

After each of the above, specimens were prepared using established techniques.[11]

Interlaminar shear strength coupons   Interlaminar, shear strength samples were manufactured using conventional laminating techniques[14,16] from the four types of glass fibres as received, and from the APS fibres, after warm-water extraction.

1) Post-cure schedules:
   The five types of laminate were cut into test pieces, then post-cured at either 50°C for 16 hrs, 90°C for 2 hrs, or 130°C for 1.5 hrs.
2) Wet samples
   Twenty ILSS test pieces were fabricated from the four types of as-received fibre tows, postcured at 130°C for 1.5 hrs and immersed in deionised water at 50°C until they reached constant weight. Ten were tested "wet".
3) Redried samples:
   The remaining ten "wet" samples were redried in vacuo at 50°C to constant weight, then tested.

The equilibrium moisture contents and the degree of leaching was calculated for each of the four types of composite.

RESULTS

The Effect of Aqueous Conditioning on Interfacial Shear Strength

In order to examine the influence of polysiloxane layers on the shear strength of

composites, the effect of fibre conditioning on τ was determined. The results are presented in Figure 2. Immersing the fibres in warm water prior to sample preparation enhanced the τ of the APS silane treated glass fibres. After extraction in boiling water, τ diminished slightly but remained higher than that for the as-received fibres. For the VTS-treated fibres the increase in τ is within the standard deviation and may not be significant. The influence of the constituents of the size could confuse interpretation of the results; however, equivalent treatments had negligible influence on the sized but non-silane treated AR-glass fibre control (NAP in Fig. 2).

The results provide empirical evidence that when adhesion promoters are deposited onto the surface of glass fibres, the silane deposit acquires a structural gradient of varying degrees of hydrolytic stability; this complements the observations of Ishida and Koenig using Fourier Transform Infrared Spectroscopy (FTIR).[2] Their analytical studies, combined with these empirical results, conclusively demonstrate that one of the components of the silane deposit on glass fibres is incompletely condensed oligomeric silanes of low hydrolytic stability, which can be extracted by warm water and whose presence is deleterious to bond formation between the inorganic glass fibre and the organic matrix. More recently, Jones and Wang[4] have confirmed that hydrolysed APS is deposited from aqueous solution as a graded deposit of differing hydrolytic stability and crosslink density.

The stability of the silane deposit increases gradually towards the fibre surface. The component, which is resistant to warm water extraction, consists of chemisorbed silanes made up of higher polymeric siloxanes; these bond more readily with the matrix. Immediately adjacent to the fibre surface, a tenacious layer, chemically bonded to the fibre surface, exists which is slightly less reactive to the matrix (Table I) and is not removed by extended extraction with boiling water.
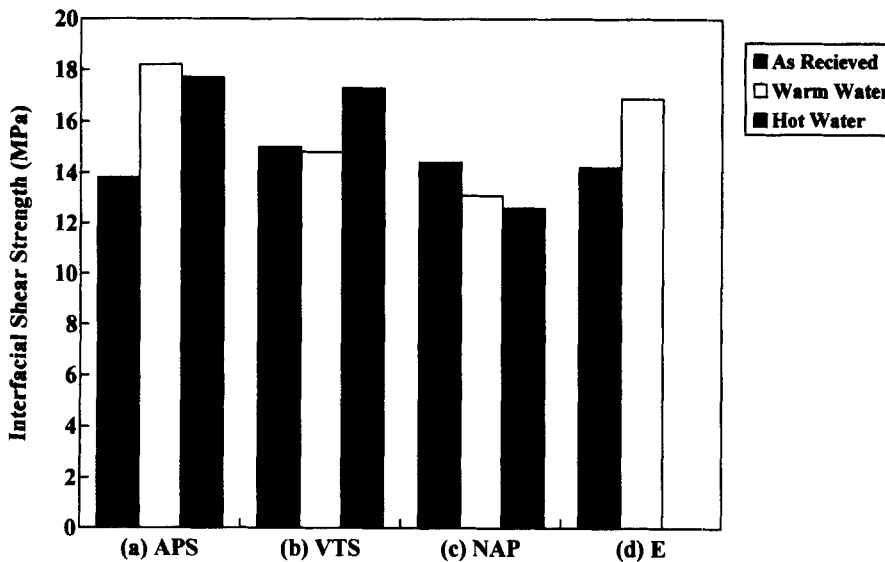

FIGURE 2 The effect of aqueous extraction on the interfacial shear strengths of AR-glass fibres with differing silane coupling agents (a) APS, (b) VTS, (c) without coupling agent, (d) E-glass control.

The VTS-treated AR-glass fibres and the E-glass fibres are both compatible with the vinyl ester matrix. Removal of weakly adsorbed oligomers from the interfacial region would allow the matrix to form a chemical link with the functional groups of the chemisorbed layers of adhesion promoter. It is difficult to interpret the coupling action of the APS *via* an amino/vinyl group reaction. However, on removal of physisorbed oligomers, the resin can diffuse into the bonded graded silane network creating a semi-interpenetrating network which could provide a mechanical key. In contrast, Cheng *et al.*[5] found that with E-glass, coupling was maintained after hot water extraction had removed all but one or two monolayers of silane and they proposed that aluminium hydroxide groups were formed which provided an acid-base adhesion mechanism. For the AR-glass fibres, the semi-interpenetrating network mechanism appears to be more-appropriate.

The Effect of Aqueous Conditioning on the Retained Interlaminar Shear Strength

In addition to providing a bifunctional chemical link between the inorganic fibres and the organic matrix, one of the prerequisites of adhesion promoters is to improve property retention of a composite under wet or corrosive environments. To achieve this, it is usually necessary to include a post-curing stage in the fabrication schedule. It was not possible to determine the influence of either post-curing or aqueous conditioning on the shear strength using the embedded single filament test, since both treatments embrittled the vinyl ester resin, preventing saturation of the fragmentation process from being achieved. Instead, the short beam shear strength test was chosen to monitor the changes occurring at the fibre-matrix interface.

Unidirectional composites were made from the four types of as-received glass fibre and the APS-treated fibres after aqueous extraction of the weakly adsorbed silane oligomers. A disadvantage of using a "real" composite system is that interpretation of the results can be clouded by difficulties in separating the influence of the conditioning on the resin properties from those of the interfacial region. This was overcome by comparing the results obtained from AR-glass fibre reinforced composites with control composites containing commercial E-glass fibres. These E-glass composites reach a constant ILSS of approximately 50 MPa, irrespective of the postcure temperature (Table II) and, furthermore, they retain 100% of this value after aqueous conditioning and redrying to constant weight (Table III).

The VTS-coupled AR-glass fibre reinforced composites achieved a similar ILSS to the E-glass control, whereas the APS-coupled ones were not so effective (Table II). This is to be expected since the formation of coupling through copolymerisation of VTS with the vinyl ester resin can occur, whereas the APS probably relies on the formation of an interpenetrating network.

Removal of the weakly adsorbed physisorbed oligomers in the APS deposit prior to lamination does impart some improvement to the ILSS (Table II); these samples achieve an equivalent shear strength to the optimised E-glass fibre ones following the low temperature post-cure. However, the ILSS was reduced after post curing at 130°C (Table II). Furthermore, the ILSS of laminates reinforced with the as-received APS fibres and the non-silane treated AR-glass fibres also decreased gradually as the post-cure temperature was increased from 50°C, to 90°C, to 130°C.

TABLE II

The effect of the curing temperature on the dry ILSS (MPa) of equilibrated
AR-glass fibre/vinyl ester composites

Curing Schedule	Specimen Type				
	APS	APS*	VTS	NAP	E
20°C-6 months	35.4 (1.6)		36.4 (1.1)	31.1 (1.3)	36.8 (1.8)
50°C-16 hrs	50.9 (2.7)	49.1 (1.2)	51.7 (3.0)	44.3 (2.2)	50.8 (4.4)
90°C-2 hrs	45.7 (1.9)	49.1 (3.4)	53.1 (3.1)	42.4 (3.3)	50.3 (3.2)
130°C-1.5 hrs	40.8 (2.1)	41.5 (1.8)	51.5 (2.1)	37.6 (2.5)	50.5 (5.0)

* Physisorbed oligormers extracted by warm water.
Figures in parentheses refer to one S.D.

TABLE III

The effect of aqueous conditioning on the ILSS (MPA) of vinyl ester composites post-cured at
130°C for 1.5 hrs

Sample Conditioning	Fibre Type			
	NAP	APS	VTS	E
Dry Control (Vacuo at 50°C to const wt)	38 (2.5)	41 (2.1)	51 (2.1)	51 (5.0)
Wet Sample (Water at 50°C to const wt)	26 (5.4)	32 (1.6)	29 (1.5)	32 (2.5)
Redried sample (Wet sample, redried at 50°C in vacuo to const wt)	38 (2.6)	37 (2.2)	33 (2.3)	52 (3.7)
Aqueous 2M H_2SO_4 at 50°C, 4 months (Washed, dried at 50°C in vacuo to const wt)	36 (4.0)	42 (2.2)	37 (1.2)	47 (5.8)

Since continuous crosslinking of the matrix should have led to an increase in the
matrix shear strength, the decrease in ILSS with increasing temperature could be
attributable to micromechanical effects in the interfacial region; ILSS the values for
the E-glass fibre reinforced composites are independent of the post-cure temperature
(Table II). This argument is further supported by the damaging effect of fibre heat
treatment at 130°C on the formation of the interface in cold-cured composites,
reinforced with APS-coated fibres; their interfacial shear strength is reduced from
11.7 to 10.1 MPa. In contrast, that of the VTS-treated fibres is unchanged (Table I).

The effect of aqueous conditioning of the fully-cured vinyl ester laminates on their
ILSS is presented in Table III. Both adhesion promoters increase the shear strength
and the wet strength retention of the AR-glass composites. However, on redrying, the
values of ILSS were lower than expected, especially for the VTS-treated fibres. In
contrast, composites reinforced with non-silane treated AR-glass fibres retained their
original ILSS on redrying to constant weight, offering improved ILSS over the two

TABLE IV

The effect of fibre type on the equilibrium water absorption (in %) of the vinyl ester composites under different postcuring schedules

Curing Schedule	Fibre Type				
	APS	APS after warm-water extraction	VTS	NAP	E
50°C 16 hrs	1.12	1.25	1.09	0.68	0.4
90°C 2 hrs	1.00	1.02	0.90	0.81	0.37
130°C 1.5 hrs	1.03	1.04	1.00	0.86	0.38

silane treated AR-glass fibre reinforced laminates. Furthermore, composites reinforced with the AR-glass fibres had higher equilibrium moisture contents than the E-glass control (Table IV), which retained its original ILSS after aqueous conditioning.

The difference between the behaviour of the AR-glass reinforced fibre composites and the E-glass fibre control suggests that the varying degrees of integrity of the interface, as determined by the ILSS and the interfacial shear strength, appear not to be solely responsible for the behaviour of AR-glass fibre reinforced composites. The surface chemistry of the interfacial region would appear to be more complex than the model proposed by Ishida and Koenig.[2]

The Surface Chemistry of the Interfacial Region

Angle-resolved XPS was used to study the chemical structure of APS, an amine functional adhesion promoter deposited onto the surface of AR-glass plates. APS was chosen specifically since nitrogen is readily detected by XPS. For industrial purposes, glass fibres are usually treated with a silane solution acidified with acetic acid to pH 3.5. However, for the purpose of the XPS analysis, the glass plates were treated with a 1.5% by weight solution of APS in deionised water. This has two advantages, the surface chemistry is simplified and a thicker layer of silane is deposited at this concentration.[17] The silane deposit was subjected to equivalent treatments used for the mechanical testing programme, thus providing a thorough chemical analysis of the interfacial region (Tables V–VII). For comparative purposes, the glass plates were also treated with an organic solution of APS in Analar methanol of equivalent concentration.

Survey scans were undertaken using a 45° take-off angle, followed by narrow scan spectra for each element at 15°, 30° and 45° relative to the plate surface. This determined the elemental structural gradient over the analytical depth of about 3–5 nm. The calculated atomic percentages are presented in Table V. Carbon has not been included in the calculation because its presence as a contaminant leads to interpretational difficulties. For example, uncoupled glass fibres which had been heat cleaned to 600°C to remove the size prior to analysis were still contaminated with carbon.

TABLE V

Relative Atomic Surface Composition (%) of AR glass slides with and without APS coating determined by angle resolved XPS

	As-polished			Heat-cleaned at 200°C			Aqueous coated			Methanol coated		
Analysis Angle relative to surface /°	15	30	45	15	30	45	15	30	45	15	30	45
Element												
Si	17.7	17.8	15.0	22.3	19.8	12.4	24.3	23.8	22.4	28.6	28.3	25.8
Zr	2.7	4.2	3.7	0.6	1.9	2.4	4.0	5.3	5.8	0.4	—	—
Ca	—	—	1.9	—	—	2.2	—	—	3.9	—	—	—
O	75.9	75.7	76.8	72.2	76.7	79.1	66.0	58.2	58.6	50.3	51.7	54.7
Na	3.7	2.2	4.5	4.9	1.6	4.1	2.8	0.4	1.3	0.6	0.3	1.7
N	—	—	—	—	—	—	2.9	12.3	8.0	20.0	19.7	17.8

TABLE VI

Effect of aqueous extraction at 50°C and heat treatment on the relative atomic surface composition (%) of silanised AR glass slides at differing analysis angles

	Heat-cleaned		As-coated Heated at 130°C			As-coated warm-water extracted			As-coated Warm-water extracted then heated at 130°C		
Angle relative to surface /°	15	45	15	30	45	15	30	45	15	30	45
Element											
Si	23.2	22.9	24.2	27.0	24.5	21.4	23.0	24.2	24.5	28.3	22.5
Zr	—	4.4	0.3	0.9	1.8	4.2	4.7	5.8	1.7	1.8	3.1
O	72.5	67.7	70.2	64.3	67.6	71.0	71.2	67.2	68.7	65.6	69.2
Na	4.3	5.1	2.1	4.0	5.4	—	0.02	0.25	2.6	3.0	2.5
N	—	—	3.2	3.7	0.5	3.3	1.0	2.7	2.5	1.5	2.8

TABLE VII

Effect of aqueous extraction at 100°C and heat treatment on the relative atomic surface composition (%) of silanised AR glass slides at differing analysis angles

	As-coated hot water extraction			As-coated hot water extraction then heat treated at 130°C		
Analysis Angle relative to surface/°	15	30	45	15	30	45
Element						
Si	18.1	20.0	18.9	12.5	10.7	15.1
Zr	2.4	2.7	4.2	13.8	15.9	15.4
O	72.1	71.0	72.0	70.4	67.8	65.3
Na	0	0	0	1.8	1.8	1.8
N	7.4	6.1	4.9	1.5	2.9	2.5

Wang and Jones[4] have estimated that the sampling depths for the Nls photoelectron associated with take-off angles of 15, 30 and 45° are $2.3 \pm 0.2, 4.5 \pm 0.4$ and 6.4 ± 0.5 nm, respectively.

The structural gradient of the APS was determined by following the nitrogen concentration relative to the other elements, as a function of analysis depth. The nitrogen surface concentration is directly proportional to the number of amino-silane molecules deposited onto the glass substrate. This was confirmed by analysing a non-silane treated AR-glass plate on which the nitrogen ions could not be detected by XPS; Wang and Jones have demonstrated the applicability of this technique to other types of glass surface[4] and fibres.[18]

Furthermore, these adhesion promoters condense to higher oligomers within an organic solution than in an aqueous one and, therefore, deposit a thicker poly-siloxane film onto the substrate.[19] XPS confirmed that approximately twice as much APS was deposited onto the glass plates from Analar methanol than from the deionised water of equivalent concentration (Table V). The deposit from organic solution contained a negligible zirconium count, indicative of a silane film of at least 6 nm thick, the maximum analysis depth of XPS. As indicated by the invariant nitrogen concentration, the number of amine groups remained approximately constant through its thickness. In contrast, the deposit from aqueous solution was characterised by a through-thickness variation in the nitrogen concentration (Table V).

Thus, the organo-functional groups of the adhesion promoters required for matrix compatibility were masked or buried beneath the surface. The silane interface of the aqueous deposit on the AR-glass plates is characterised by the presence of sodium ions (Table V). Sodium oxide comprises approximately 14% of the AR-glass structure. It is known that sodium ions can be readily leached from the surface by aqueous solutions[20] and XPS demonstrates that sodium ions rapidly diffuse to the surface of untreated glass plates (Table V). The driving force for the movement of these interstitial species is provided by the high surface energy of the glass surface and its thermodynamically-favoured reduction by the concentration of the alkali and alkali-earth oxides at the surface. The sodium ion profiles, within the silane coatings determined by XPS (Table V), would suggest that the deposit from the aqueous solution has a less dense structure than that from the organic solution and/or that during aqueous treatments, sodium ions leached from the surface become trapped in the siloxane deposit. We have examined the density of the siloxane coatings elsewhere,[4,14] and the mobility of the sodium ions within the siloxane gradients by heat treating an aqueous extracted silanised glass plate. As can be seen in Tables V and VII and Figures 3 and 5, sodium rapidly diffuses from the substrate into the silane layer on reheating; therefore, we favour the diffusion rather than entrapment of sodium ions.

The deposit from aqueous solution had a higher zirconium count than the untreated AR-glass plate (*i.e.*, the heat cleaned sample) and that silanised in methanol. The errors associated with XPS analysis are $\sim 10\%$, so that the enhance ment of the Zr concentration of the aqueous silanised plate is significant. The lack of calcium in the 30° surface analysis which can be considered to be indicative of the substrate, indicates a silane thickness of ≈ 5 nm. The 12.3% N is also consistent with a thickness of this magnitude. Thus, it would appear that zirconium could have been leached from the glass surface and incorporated during the aqueous coating pro-
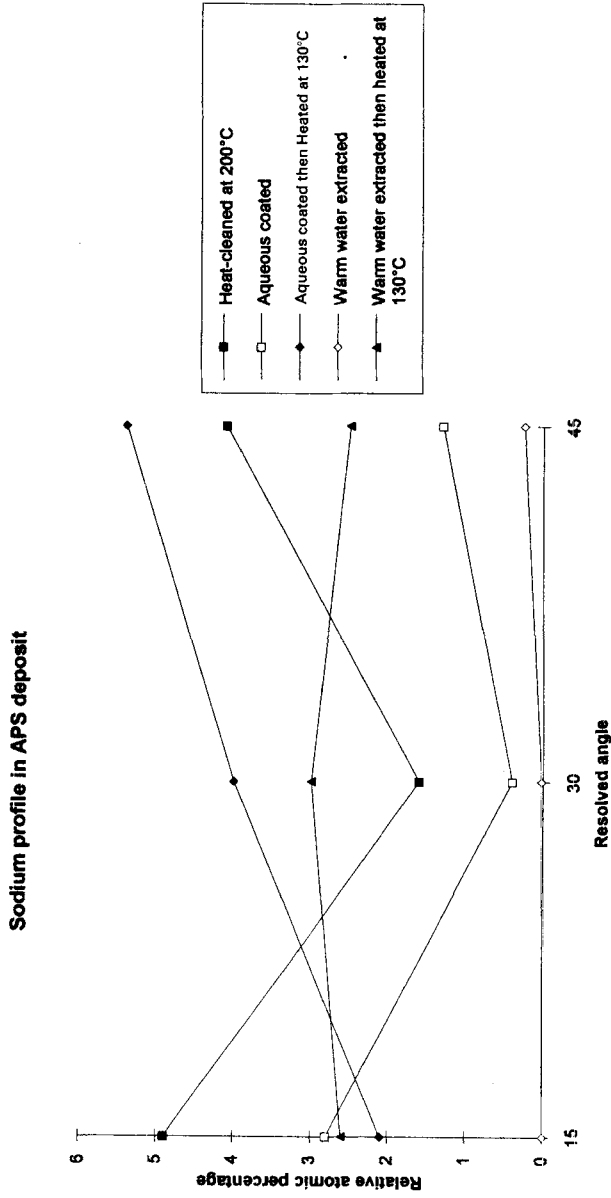
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FIGURE 3   Sodium cation concentration profiles in the APS deposit on an AR-glass surface before and after aqueous extraction, at 50°C and subsequent heating at 130°C. 15° analysis angle represents the air/silane interface.
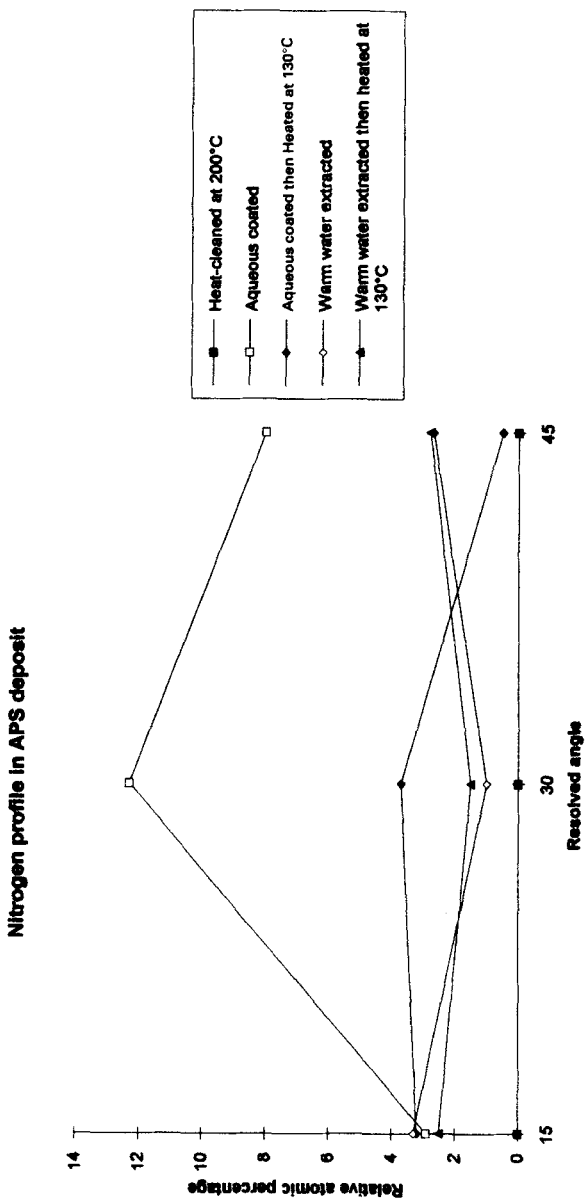
FIGURE 4 Nitrogen concentration profiles in the APS deposit on an AR-glass surface before and after aqueous extraction at 50°C and subsequent heating at 130°C.

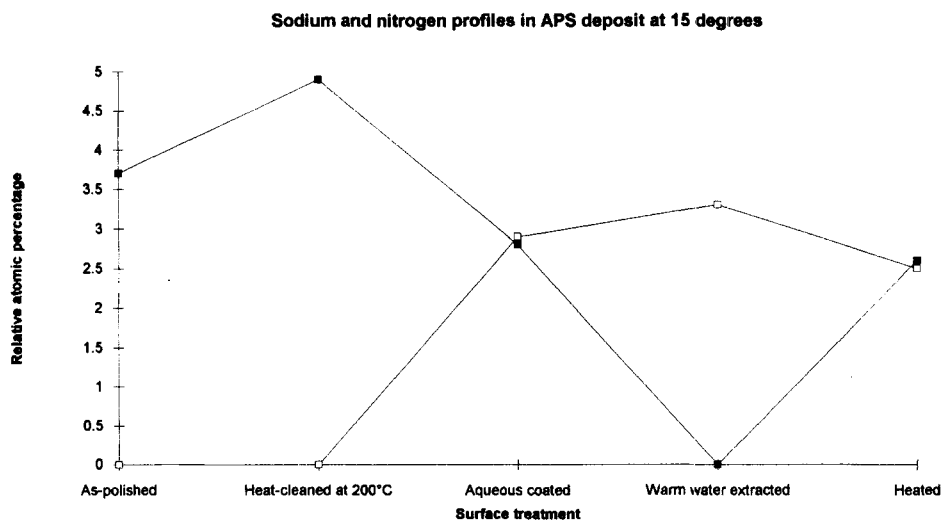**Sodium and nitrogen profiles in APS deposit at 15 degrees**

FIGURE 5   Comparison of sodium and nitrogen atomic concentrations at the air/silane interface for the sequence of treatments showing the effect of heating on the mobility of the sodium cation: ■ Na, □ N.

cedure. Boerio et al.[21] reported that the amino-silane etches the surface oxide film of aluminium substrates; aluminium incorporation into silane deposits on E-glass have also been reported.[4] Recent static secondary ion mass spectrometric studies have also indicated that, boron from E-glass, as $B(OH)_3$ polymers, may also be involved in APS coating.[22] It is possible that under the alkaline conditions, which exist locally by sodium ion dissolution, zirconate ions are leached from the glass surface and become trapped in the polysiloxane structure either chemically or physically. Since the sub-surface zirconium concentration, which approximates to the bulk, as determined by XPS analysis of the as-polished plate at a 45° take-off-angle, is 3.7%, a surface reaction seems the most likely mechanism. Larner et al.[23] used XPS to study the precursor to AR-glass, namely G 20 glass. They reported that the concentration of zirconia at the surface of G 20 fibres increased after conditioning in an aqueous cement extract. The precise nature of the zirconium compound was not ascertained. However, it was suggested that it could be a sodium zirconate or sodium zirconate hydrate.

The results of Larner[23] are consistent with the data in Table VI where, after warm water extraction at 50°C, enrichment of the surface zirconium concentration relative to the heat-cleaned plate has occurred. In addition, in Table VI, it is seen that heat treatment after extraction leads to a reduction in the zirconium concentration as a result of sodium ion migration to the surface.

After hot water extraction (Table VII) and subsequent heat treatment, extensive reorganisation of the surface chemistry has occurred as a result of sodium migration.

Further confirmation of the complexity of the surface chemistry of the interfacial region adjacent to the AR-glass fibres is provided by the higher calcium count within the aqueous-coated deposit on the glass slide relative to the heat-cleaned starting material (Table V).

In the model experiments, APS was deposited from an aqueous solution of pH = 10.6. In contrast, during commercial fibre coating, an acidic media of approximately pH = 3.5 would have been used to hydrolyse the adhesion promoter within the sizing/emulsion. However, the mobility of the sodium ions, as demonstrated in Tables V–VII, would ensure that alkaline conditions, not too dissimilar to the aqueous media employed in these, probably exist at the fibre surface in the commercial process.

DISCUSSION

An integrated study involving interface characterisation using the embedded single filament tensile test and the short beam shear strength test has been carried out together with a analytical examination of a model of the fibre surface chemistry using angle-resolved XPS. In this way the effect of the chemical structure of the interfacial region on the performance of composites has been examined.

In previous studies[18] we have compared the analyses from silanized E-glass fibres and plates and demonstrated the validity of extrapolating data from polished surfaces to commercial fibres. The major complication with fibres proved to be the presence of silane contaminants. However, as shown in Tables V–VII, reorganisation of both surfaces occurs in aqueous environments.

The single embedded filament test showed that the as-received shear strength of APS-treated AR-glass fibre vinyl ester composites is low (Table I). XPS has demonstrated that the functional groups required for compatibility with the matrix are buried in the surface layers and that sodium, zirconium and possibly calcium may exist within the polysiloxane deposit. After warm-water extraction, the profile of the silane deposit is altered, with a greater proportion of the remaining amine functional groups made available at the air/silane surface for co-reaction with the matrix (Fig. 4 and Table VI); this is beneficial to bond formation between the vinyl ester matrix and the reinforcing fibres (Table I) and explains the enhancement in interfacial shear strength given in Figure 2.

The majority of the sodium ions in the deposit are also removed by the warm-water extraction (Table VI). Similarly, hot-water extraction leads to an enhancement of the air/surface nitrogen concentration (15° angle in Table VII) and a reduction in sodium levels. The former contributes to the maintenance of interfacial shear strength shown in Figure 2.

The relative atomic percentages measured at the 45° take-off angles for the APS-treated plate (Table V) are representative of the average composition through the APS deposit and incorporate a contribution from the AR-glass surface; in contrast, that at the 15° take-off angle only indicates the relative atomic structure of surface of the APS deposit alone.[4] The zirconium level appears to be unchanged after warm-water extraction (Table VI). However, the extraction reduces the thickness of the APS deposit, as shown by the lower nitrogen concentration, and the zirconium count measured at 15° could, therefore, include a contribution from the substrate as well as from within the APS deposit. However, the remaining zirconium component does not appear to be deleterious to bond formation.

The low density interphase of the APS-treated AR-glass fibre reinforced composite is subject to thermal degradation during post-cure, as shown by the reduction in ILSS (Table II) and the damaging effect of fibre heat treatment on the formation of the interface in cold-cured composites (Table I). The full reasons for the decrease in shear strength are uncertain, but possible mechanisms are discussed.

XPS has demonstrated the presence of sodium ions within the interphase. These are removed by aqueous extraction but can be detected after heat treatment for a time and temperature equivalent to post-curing (Fig. 3 and 5), thus confirming their mobility within the silane deposit; the silane concentration is largely unaffected (Tables V, VI and VII). Figure 1a shows that heat treatment of a polished plate also causes sodium cations to diffuse to the surface.

It is known that the re-equilibration of oligomeric and polymeric linear siloxanes occurs by base catalysis[24] during thermal treatment as a result of the thermodynamic equilibrium between polymers and oligomers. Therefore, during post-curing of the composites, the interphase region can be weakened by the partial depolymerisation of the network siloxane; the net effect would be a reduction in interfacial bond strength which is observed (Table II). Extraction of the APS oligomers from the fibres with warm water enhances the ILSS (Table II), but subsequent post-curing of the composite at 130°C results in a reduction. This experimental result also supports the argument that thermal degradation of the interphase region in the composite occurs through base-catalysed depolymerisation of the polysiloxane coupling layer at the fibre interface. An alternative mechanism could involve an increase in the crosslink density of the siloxane network at the interface, reducing the efficiency of the bonding mechanism. However, this would have to occur after any interpenetrating network will have formed during the initial curing cycle and lead to an improvement rather than a decrease in adhesion. Other explanations such as amine group or base-catalysed degradation of the matrix is expected to occur with E-glass composites and this has not been reported elsewhere. The resistance of a cured vinyl ester resin to alkalis is generally good and would need the presence of water for hydrolysis to occur. On the other hand, siloxane equilibration reactions can occur in the absence of moisture.[24]

In contrast, the composites reinforced with VTS-treated AR-glass fibres are not influenced by the post-cure temperature and have a comparable performance to the E-glass control. This demonstrates the benefit of the co-polymerisation between the vinyl functional groups of the adhesion promoter and the vinyl ester resin, where much higher degrees of thermal degradation are required to have a significant effect on the ILSS. Furthermore, Ishida and Koenig[2] reported that the VTS coating was more resistant to hydrolysis and concluded from a kinetic argument that it was highly crosslinked. This would imply that the ceiling temperature of this polysiloxane is high, making thermal re-equilibration less likely. In any case, from a kinetic standpoint a higher degree of bond scission would be required for the effect to be noticed.

The four types of composites were subjected to the environmental conditioning outlined in Table III. The retained shear strengths of both silane-treated AR-glass fibre reinforced laminates were inferior to the E-glass control, which achieved its original shear strength after aqueous conditioning. The higher water absorption by the coupled AR-glass fibre composites (Table IV) implies that the water is located

TABLE VIII

Extent of leaching as determined from the weight loss on drying, after immersion of composites ($V_f = 0.45 \pm 0.02$) in water at 50°C to equilibrium

Curing Schedule	Fibre Type			
	APS	VTS	NAP	E
50°C 16 hrs	0.29	0.19	0.39	0.08
90°C 2 hrs	0.15	0.08	0.22	0.06
130°C 1.5 hrs	0.13	0.03	0.12	0.03

within the silane-rich interphase. The removal of the oligomeric component from APS-coated fibres had no effect on the moisture absorption of the composites. Also, the fact that the extent of leaching remained constant after post-curing at 90 and 130°C (Table VIII) confirms that the water absorption and the tendency to lose weight after redrying is related to chemical changes which occur during post-curing. Therefore, the presence of the sodium ions would appear to contribute to these effects especially since E-glass, which contains a significantly lower proportion of sodium oxide, is unaffected.

The vinyl silane deposit is known to be highly crosslinked[2] and could act as a semipermeable membrane, entrapping mobile sodium and related ions but allowing water molecules to pass through. Sodium ions would increase the pH within the interphase and lower the wet bond strength of these composites. On redrying, the pH would increase further as the sodium ion solution becomes more concentrated. Chemical degradation of the interphase could cause fibre matrix disbondment; it is well known that the hydrolysis of siloxane bonds is base catalysed. This would account for the low retained ILSS of the VTS composites given in Table III. Further evidence for this mechanism appears in Table III where it is seen that the retained ILSS after immersion in aqueous 2M sulphuric acid is better than after water treatment, in contrast to the E-glass composites.

One of the most unexpected results was the full retention of the original ILSS for composites reinforced with the non-silane treated AR-glass. This could arise because the ILSS of the dry non-coupled composite arises predominantly from a mechanical bond through friction. The equilibrium moisture content of the cast vinyl ester resin cured in vacuo at 50°C to constant weight was found to be 1.33%. The fibre volume fraction of the composites was 0.45 ± 0.02, which gives a theoretical moisture absorption of 0.73%. The equivalent leaching from an ideal composite would be 0.1%. This should be compared with the experimental degrees of leaching for the composites cured at 50°C (Table VIII), Thus, moisture absorbed by the composites containing the non-coupled fibres (NAP) appears to be located mainly in the matrix. Therefore, the reduction in ILSS (Table III) can be attributed to matrix swelling which reduces the thermal contractive stresses responsible for the mechanical adhesion. On redrying, the mechanical bonds reform.This is in contrast to the coupled fibres where the interphase will have semipermeable characteristics and an ability to ac-

comodate absorbed moisture. The embedded single filament test has been used to demonstrate that the bond between the non-silane treated fibre and the vinyl ester resin is predominantly a physical one.[11] The lower water absorption by this composite (Table IV) supports the argument that the presence of sodium cations in the interphase region is responsible for the enhanced moisture absorption of composites containing silanised AR fibres. Therefore, it can be concluded together with the results of the XPS study that sodium ion diffusion into the siloxane interphase during fibre coating creates a region in which the sodium ions are finely dispersed, which will be particularly active in the presence of water. Consequently, the rate of degradation of the interface will be increased.

These observations are backed up by the behaviour of the E-glass fibre reinforced control which contains a significantly lower proportion of sodium oxide. Initially, the ILSS is similar to the AR-glass fibre composites, but the control absorbs much less water and retains its original shear strength after aqueous conditioning and redrying.

From the above it is clear that sodium cation involvement with the silane component of the fibre sizing has a profound influence on the properties of the composite. Therefore, a consideration of the mechanisms involved is relevant. Watts and Chehimi[25] have examined the diffusion of sodium cations from soda-lime glass surfaces into polymeric overlayers. Using the Lewis acid concept they obtained a correlation between the concentration of sodium in the polymer and its basicity. In this case, the polymer films were peeled away from the substrate before analysis by XPS so that any uncertainties associated with analysis depth and substrate contribution were absent. Na^+ is a Lewis acid and was found to diffuse from the glass into polymers which were Lewis bases but not into polymeric Lewis acids. The driving force for Na^+ diffusion was considered to be the acid-base interaction between itself and the polymer. Na^+ is a hard acid because of its small size and large positive charge.[26] Thus, the harder the base the stronger the interaction. For the polymers at the glass interface in these composites, their basicity is considered to decrease in the following order; poly(hydrolysed APS) > poly(hydrolysed VTS). The mechanism of the durability of these AR composites is complex, but the acid-base argument provides a fundamental explanation of some of the phenomena reported here.

CONCLUSIONS

The embedded single filament test was used in conjunction with XPS to demonstrate that the low shear strength of as-received, APS-treated AR-glass fibre composites was due to the presence of mobile sodium ions within a weak physisorbed region. In addition, the functional groups required for compatibility with the matrix are buried in the surface layers.

Warm water extraction enhanced the bond strength of the three silane-treated glass fibres. Surface analysis demonstrated that this removes the soluble physisorbed oligomers and the majority of the hygroscopic sodium ions from the APS deposit. Furthermore, the functional groups are made available at the air/silane surface for co-reaction with the matrix.

Subsequent heat treatment for a time and temperature equivalent to post-curing leads to a recovery in the surface sodium ion concentration, confirming the mobility of the sodium ions within the polysiloxane deposit.

A tenacious polysiloxane layer exists adjacent to the glass surface of the silane-treated fibres. This could not be removed by extended extraction in boiling water and is slightly less reactive to the matrix.

The low density interphase of the APS-treated AR-glass fibre reinforced composite is subject to thermal degradation during post-cure. This was attributed to base-catalysed re-equilibration of oligomeric and polymeric siloxanes which occurs because of the thermodynamic equilibrium between polymers and oligomers. This results in a reduction in interfacial bond strength because the mechanism of adhesion appears to involve semi-interpenetrating network formation which is susceptible to siloxane reorganisation.

The equilibrium moisture content for all the AR-glass fibre reinforced composites is higher than for the E-glass control and is inversely related to the retained shear strength on redrying. This implies that water can be located within the silane-rich interphase as a result of the presence of the sodium ions. Following the arguments of Watts and Chehimi[25] diffusion of sodium cations from the substrate can be accounted for by an acid-base mechanism.

Acknowledgements

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