XPS and AFM Study of Interaction of Organosilane and Sizing with E-Glass Fibre Surface

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Organosilanes are often used in commercial sizings for glass fibres to provide wettability with the resin and promote strong interfacial adhesion to the matrix in a fibre reinforced polymer composite. The silane treatment is introduced as part of a complex deposition from an aqueous emulsion immediately at the spinaret and determines the optimum properties of the cured composite. To understand the interaction of organosilanes contained in sizings for glass surfaces, XPS was used to investigate the adsorption of γ-aminopropyltriethoxysilane (APS) from a simple sizing system containing a polyurethane (PU) film former. It has been found that both APS and the sizing (containing APS and PU) deposits on E-glass fibre surfaces contained components of differing hydrolytic stability. The differences observed in the AFM images of APS coated E-glass fibres before and after water extraction also confirmed that the APS deposit contained components with different water solubility.

1. INTRODUCTION

Glass fibres are widely used in the manufacture of structural composites. They exhibit useful bulk properties such as hardness, stability, and resistance to chemical attack, as well as desirable fibre properties such as strength, flexibility, and stiffness [1]. E-glass, principally developed for its excellent electrical properties, has become the universal

glass for fibre reinforcement because of its excellent chemical durability and relatively low cost. Nowadays, more than 99% of glass fibres are made from E-glass [2]. Since glass fibres have a highly polar surface, whereas matrix polymers tend to be non-polar, the fibre surface needs to be made hydrophobic to increase the fibre-matrix interaction.

Sizings are processing and performance aids, which are applied to all glass fibre reinforcements. Organosilanes, containing a polymer-compatible organic group and three hydrolysable alkoxy functional groups, are widely used in commercial sizings to provide increased compatibility of the fibres and to promote the adhesion between glass fibre surfaces and the matrix in a glass fibre reinforced polymer composite [3].

Since the 1960's [4], FTIR, nuclear magnetic resonance (NMR), XPS, and secondary ion mass spectrometry (SIMS) have been used extensively to characterize the molecular structures and reactions of silane coupling agents in solution and at composite interfaces. The interactions between organosilane/sizing and glass surfaces are shown to be quite complex, and in general, depend on the substrate surface, the solution concentration and pH, and the drying conditions [5–9].

For nearly a decade, AFM has also been successfully used to characterise the surface of glass fibres coated with different silane coupling agents and sizings [10–12]. In general, these coatings usually lead to a kind of island topography, the dimensions of which vary with polymer deposition conditions, such as concentration, time, and temperature.

In this article, XPS and AFM were employed to investigate the interaction of γ-Aminopropyltriethoxysilane (APS) with an E-glass fibre surface. APS was studied because of its wide ranging applications as well as the presence of a nitrogen atom which enables a detailed surface analysis by XPS. Extraction treatments were performed to investigate the components of differing hydrolytic stability at the silane-glass interface. A simple sizing system containing both polyurethane (PU) and APS was used to understand the role of silane in the sizing on a glass fibre surface and the influence of glass surface chemistry on the structure of sizing deposit.

2. EXPERIMENTAL

2.1. Materials and Sample Preparation

APS (GE Speciality Materials, Meyrin, Belgium) with the structure of $NH_2-(CH_2)_3-Si-(OC_2H_5)_3$ was used for treating unsized E-glass

fibres (Owens-Corning, Granville, OH, USA). APS was hydrolytically dissolved in deionised water at a concentration of 1% by weight. The solution had a natural pH of 10.6. The unsized E-glass fibres were immersed in the 1% APS solution for 15 min at room temperature. The coating conditions were chosen for the deposition of a representative hydrolysed silane coating. After silanisation, the glass fibres were allowed to dry in a desiccator at room temperature before transferring to an oven at 100°C for 2 h. These fibres are referred to as APS coated.

Some of the APS coated fibres were extracted by immersion in deionised water at 50°C for 24 h in an oven and dried in a vacuum oven at 50°C to remove the physisorbed silane layer. These fibres are referred to as warm water extracted. Some of them were further extracted in hot water at 100°C for 2 h to remove loosely chemisorbed silane and dried in a vacuum oven at 50°C and are known as hot water extracted fibres.

Chopped E-glass fibres sized with a PU containing APS (123D, Owens-Corning, Granville, USA) were also investigated in this study. Acetone extraction was performed by immersion at room temperature for 24 h in order to remove PU and physisorbed silane layers in the sizing. These fibres were washed with deionised water three times. Some of them were dried in a vacuum oven at 50°C and called acetone extracted chopped E-glass fibres. The others were further extracted in hot water at 100°C for 2 h to remove loosely chemisorbed silane layers before drying in vacuum at 50°C. These are referred as hot water extracted chopped fibres.

2.2. XPS

XPS was carried out using a Kratos AXIS ULTRA spectrometer (Kratos Analytical Ltd., Manchester, UK). A monochromated Al Kα X-ray source with an energy of 1486.6 eV was used at 15 mA emission current and 10 kV anode potential. The ULTRA is used in fixed analyser transmission (FAT) mode, with a pass energy of 160 eV for wide scans and a pass energy of 40 eV for high resolution scans. All XPS spectra were recorded at take-off angles of 45° and 90° relative to the sample surface. The analysis chamber pressure is typically maintained between 1×10^{-8} and 1×10^{-10} torr by a turbo pump. Data analysis and charge correction were carried out using CasaXPS (software). All spectra were corrected for different levels of sample charging by shifting the C1s peak to a binding energy of 285.0 eV, corresponding to hydrocarbon groups. A linear baseline was applied to all spectra. Symmetrical peaks were used with a mixed peak-fitting function of 70% Gaussian and 30% Lorentzian for all peaks.

For analysis, chopped glass fibres were adhered in parallel to a sample stub using double sided tape. Continuous glass fibres were oriented so that they were aligned parallel to the analyzer and held in place with a stainless steel plate holder and clamp plate.

2.3. AFM

AFM was performed using a DI 3000 Scanning Probe Microscope (Digital Instrument, Veeco, Santa Barbara, CA, USA) operating in the tapping mode. Tapping mode was chosen because it eliminates lateral forces and damage to soft samples imaged in air and improves lateral resolution on samples compared with contact and non-contact AFM [13]. A tapping mode etched silicon probe (TESP300, mpp11100) cantilever with symmetric tip was used to acquire images in air at room temperature. The spring constant of the cantilever (k) was $40\,N/m$ and the nominal resonant frequency was $300\,kHz$.

The images of glass fibres were taken at the same area with scan size of $1 \times 1\,\mu m$. The data scale of $5\,nm$ was used according to the features on the glass surface. 2-D images were used to represent the E-glass surfaces.

The roughness of the surface was determined for the entire image. The root mean square (RMS) roughness was used to quantify the surface roughness, which is the standard deviation in the height in the Z-direction (Z value) within a given area [14]:

$$RMS = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{\mathrm{ave}})^2}{N}}, \tag{1}$$

where Z_{ave} is the average Z value within the given area, Z_i is the current Z value, and N is the number of points within a given area [14]. The range of Z values within an image can also be used to describe the features on the glass fibre surfaces as given by the maximum vertical distance between the highest and lowest data points [14].

3. RESULTS

3.1. Surface of Unsized E-Glass Fibre

A typical wide scan spectrum at a take-off angle of 45° from the unsized E-glass fibres is shown in Fig. 1. Silicon, oxygen, calcium, aluminium, magnesium, sodium, and boron are the main elements in an unsized E-glass fibre surface. The surface composition of these unsized

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FIGURE 1 XPS wide scan spectrum of unsized E-glass fibres.

E-glass fibres is given in Table 1. The surface of the E-glass fibres exhibited an apparent carbon contamination, of 19.5% which decreased to 8.8% with the increase in take-off angle to 90°.

The high resolution C 1s peak from the unsized E-glass fibres at a take-off angle of 45° is fitted as shown in Fig. 2. The surface carbon is associated with 67% C–C/H, 20% C–O–C/H, 5% C=O/O–C–O, and 8% of O–C=O ester/carboxylic acid species.

E-glass fibre surface and bulk compositions are shown in Table 2. We have extensively examined the carbon contamination on a range

TABLE 1 Atomic Concentrations of Unsized E-Glass Fibres Determined from the Wide Scan Spectrum at a Take-Off Angle of 45°

Elements	Atomic concentration (%)
C	19.5
Si	16.3
O	51.2
Ca	4.0
Al	5.0
Mg	0.7
Na	0.4
B	2.9

FIGURE 2 High resolution C 1s spectrum from unsized E-glass fibres.

of relevant surfaces using differing XPS instrumentation and confirmed the magnitude on water sized or unsized glass fibres. The sensitivity factors have also been calibrated for the individual instruments [15]. Figure 2 shows that 33% of the C contamination is associated with oxygen. Thus, 8.2% of the oxygen can also be attributed to carbonaceous contamination (O_C). Therefore, for comparison with the bulk composition data obtained by XRF (obtained by D. Norga

TABLE 2 A Comparison of the Relative Atomic Compositions of E-Glass Fibre Surface and Bulk

Elements	Atomic composition of E-glass Fibre (%)	
	Surface analysis[†]	Bulk analysis[*]
Si	22.5	18.9
O	59.5	61.9
Ca	5.5	6.5
Al	6.9	6.0
Mg	1.0	2.2
Na	0.6	0.3
B	4.0	4.1

[*]Bulk analysis from D. Norga and V. Kempenaer (Battice European Testing Lab using XRF).

[†]Surface analysis corrected for C contamination and the oxygen associated with this carbon (O_C).

and V. Kempenaer in Owens-Corning Battice European Testing Laboratory), the glass composition was corrected for the carbon contamination observed by XPS surface analysis at the take-off-angle of $45°$ and the oxygen associated with the O_C. The concentrations of calcium and magnesium are lower on the surface than in the bulk of E-glass fibres; however, the aluminium concentration is slightly higher on the E-glass fibre surface. The errors associated with these analyses are those typically of XPS quantification and can be estimated at 5%.

3.2. Surface of APS Coated E-Glass Fibre

3.2.1. XPS Analysis of 1% APS Deposit on E-Glass Fibre

The XPS data from APS deposits on E-glass fibres are compared with water extracted samples in Table 3. The signals for aluminium and calcium from the E-glass substrate, as well as the nitrogen from APS, are observed on 1% APS coated, warm water and hot water extracted E-glass surfaces. The ratio of N : Si for all these surfaces is lower than 1 for hydrolysed aminosilane, indicating that the thickness of the APS coating formed on E-glass fibre is less than the analysis depth of XPS. Therefore, all the signals in the XPS spectra can be attributed to both the APS deposit and the E-glass fibre.

After warm water extraction, the concentrations of carbon and nitrogen from APS as well as the ratios of C : Si and N : Si decrease

TABLE 3 Comparison of Surface Composition of 1% APS Coated and Water Extracted E-Glass Fibres Determined from Wide Scan Spectra at a Take-Off Angle of $45°$

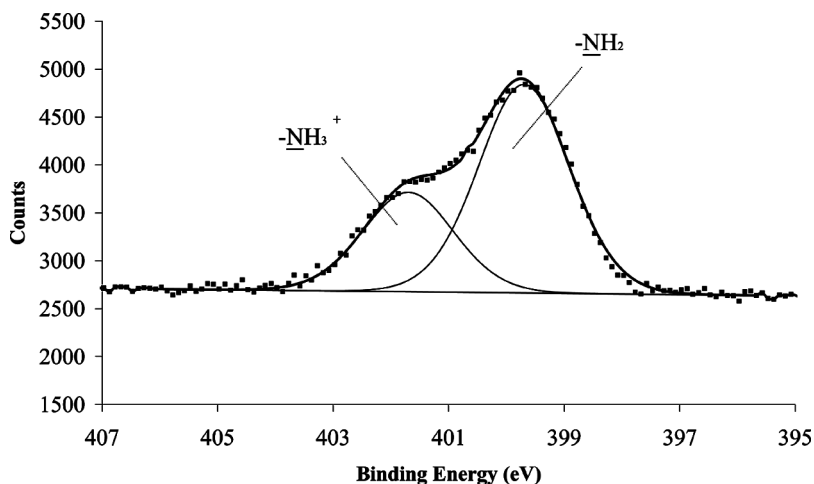|	Atomic concentration of surface elements (%)		
Elements	1% APS coated E-glass fibres	1% APS coated E-glass fibres after warm water extraction	1% APS coated E-glass fibres after hot water extraction
C	34.0	19.2	18.8
Si	15.7	17.6	18.0
O	38.0	51.6	50.7
Ca	1.7	2.2	2.4
Al	3.3	5.0	5.3
Mg	0.0	0.6	0.8
Na	0.3	0.0	0.0
B	1.3	1.6	1.9
N	5.7	2.2	2.1
C : Si	2.2	1.1	1.0
N : Si	0.36	0.13	0.12

FIGURE 3 High resolution N 1s Spectrum from 1% APS coated E-glass fibres.

significantly; meanwhile, the concentrations of Ca and Al from the E-glass fibre substrate increase. It indicates that part of the APS deposit has been extracted and more of the glass substrate has been exposed. The warm water soluble components are mainly the residual hydrolysed APS molecules between fibres in the fibre bundle and also the physisorbed APS coating on E-glass fibre surface. After hot water extraction, the nitrogen concentration and the ratios of C : Si and N : Si decrease only slightly.

The high resolution N 1s spectrum can be fitted with two components (Fig. 3), which are assigned to free amino groups ($-NH_2$) at a binding energy of 399.7 eV and protonated amino groups ($-NH_3^+$) at a binding energy of 401.7 eV. Table 4 shows that the intensity of protonated amino groups ($-NH_3^+$) on 1% APS coated E-glass fibres increases from 36 to 59% after warm water extraction and keeps relatively stable at 60% after hot water extraction.

TABLE 4 Comparison of N 1s Core Line Results for the 1% APS Coating on E-Glass Fibres Before and After Water Extractions

	$-\underline{N}H_2$ (%)	$-\underline{N}H_3^+$ (%)
1% APS coated E-glass fibres	64	36
1% APS coated E-glass fibres after warm water extraction	41	59
1% APS coated E-glass fibres after hot water extraction	40	60

3.2.2. AFM Images of 1% APS Deposit on E-Glass Fibre

Figure 4 shows the AFM images of 1% APS coated E-glass fibres before and after warm and hot water extractions. The image size is $1 \times 1\,\mu$m with a data scale of $5\,$nm.

It is observed from Fig. 4a that 1% APS coated E-glass fibre has a heterogeneous topography of "hills" and "valleys" with a height variation (*i.e.*, image Z range) of $<6.4\,$nm. The RMS is $\sim0.32\,$nm. These hills are considered to be attributable to the residual hydrolysed
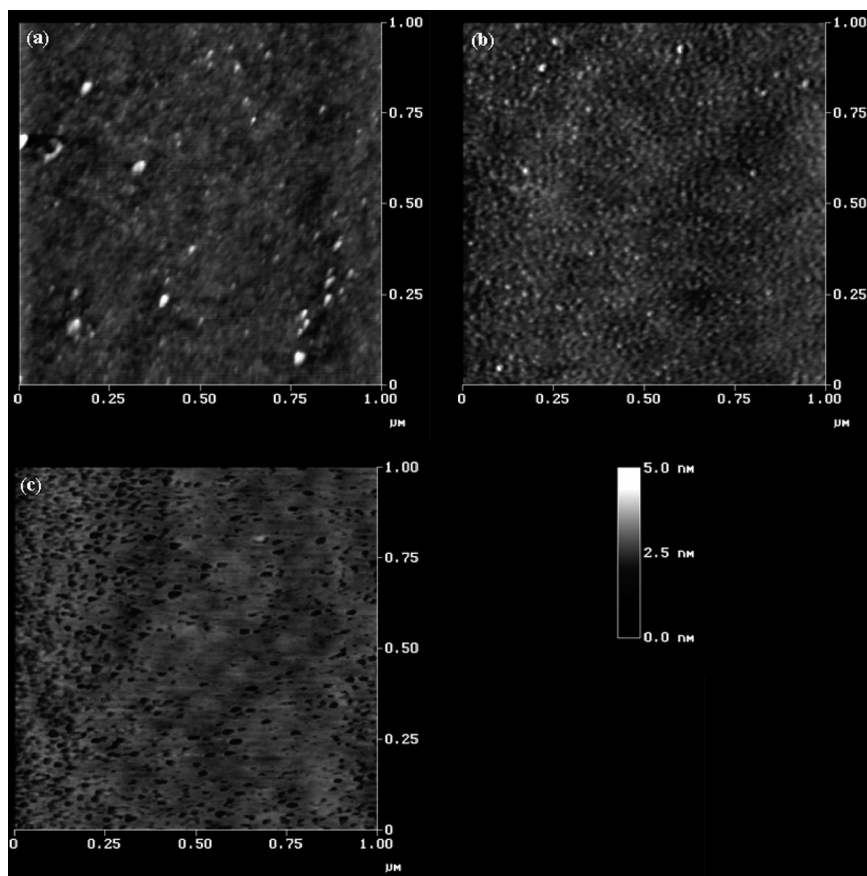
FIGURE 4 AFM images (top views) of 1% APS coated E-glass fibres before and after water extractions. (a) 1% APS coated E-glass fibre, (b) 1% APS coated E-glass fibre after warm water extraction, and (c) 1% APS coated E-glass fibres after hot water extraction. The light regions represent hills whereas the dark regions are valleys or pits as shown by the height scale.

APS molecules. The topography changes after warm water extraction as seen in Fig. 4b. The hills become relatively smaller and more uniformly distributed with a variation in height of < 4.5 nm. The possible explanation for this is the removal of the physisorbed components in the silane deposit to expose the microstructure of the chemisorbed deposit. The removal of physisorbed components is also confirmed by the XPS data in Table 3. After further hot water extraction, some "holes", "pores", or "pits" with the diameter (*i.e.*, horizontal distance) < 40 nm and height (*i.e.*, image Z range) < 2.5 nm appeared in the structure of the deposit as seen in the AFM image (Fig. 4c). The RMS is reduced to ~ 0.26 nm. According to Wang *et al.* [16,17], hot water extraction involves hydrolytic extraction of linear molecules which had previously formed the network ends. The AFM structure may reflect the random coil structure of these chains. Thus, the nanostructure which develops can be attributed to the molecular size of the extracted molecule. Another possibility is that swelling in water and constrained shrinkage on drying lead to a stress in the silane film which causes cavitation.

3.3. Surface of Sizing (PU and APS) Coated E-Glass Fibre

The chopped E-glass fibres which are coated with a full sizing (PU and APS) have been also investigated by XPS with the assistance of a model based on a patchy overlayer hypothesis [18]. Acetone was expected to dissolve the PU component and the non-crosslinked physisorbed APS oligomers from the sizing, while additional hot water extraction was expected to remove the hydrolytically soluble or loosely chemisorbed APS layer to expose the highly crosslinked or strongly chemisorbed APS deposit on chopped E-glass fibres.

The XPS data at a take-off angle of $45°$ on chopped E-glass fibres before and after extraction are compared in Table 5. Thomason and

TABLE 5 Comparison of XPS Data from Sizing Coated, Acetone Extracted, and Further Hot Water Extracted Chopped E-Glass Fibres

	Chopped E-glass fibres with PU/APS sizing (123D)		
	As coated	Acetone extracted	Further hot water extracted
C (at %)	72.1	70.8	65.6
Si (at %)	1.0	1.5	3.4
O (at %)	23.9	24.5	26.1
N (at %)	3.0	3.2	4.9

Dwight [19] have reported that the C : Si ratio from XPS analysis can be used as a first approximation for the level of organic material on the glass fibres. A ratio of C : Si below 10 indicates that the XPS signal is dominated by the glass substrate and that the coverage of organic material on the glass fibres is poor. If the C : Si ratio is above 10, then the composition of the sizing dominates the XPS spectrum and a good coverage is indicated [18]. It can be seen from Table 5 and Fig. 5 that the C : Si ratios for the chopped E-glass fibres are all in excess of 10 so that it can be concluded that the XPS data are dominated by the chemistry of the deposited sizing.

Figure 5 plots the ratios of C : Si, O : Si, and C : N from chopped E-glass fibres with PU and APS coating before and after acetone and hot water extractions. With acetone extraction, the C : Si ratio is reduced from 72.1 to 47.2 while the C : N ratio remained constant. After further extraction with hot water the silane component in the coating is apparently enriched. C : Si and O : Si ratios decrease after acetone and hot water extraction. The ratio of C : N is reduced only slightly from 24.0 on sizing coated chopped E-glass fibres to 22.1 after acetone extraction. Since the C : N ratio for polyurethane is much higher than the C : N ratio of APS, the nitrogen signal is considered to arise mainly from APS in the sizing. Thus, the slight decrease in the C : N ratio indicates that acetone extracts not only polyurethane but also some low molecular weight APS oligomers. A significant decrease in the C : N ratio would be observed only if the PU film former
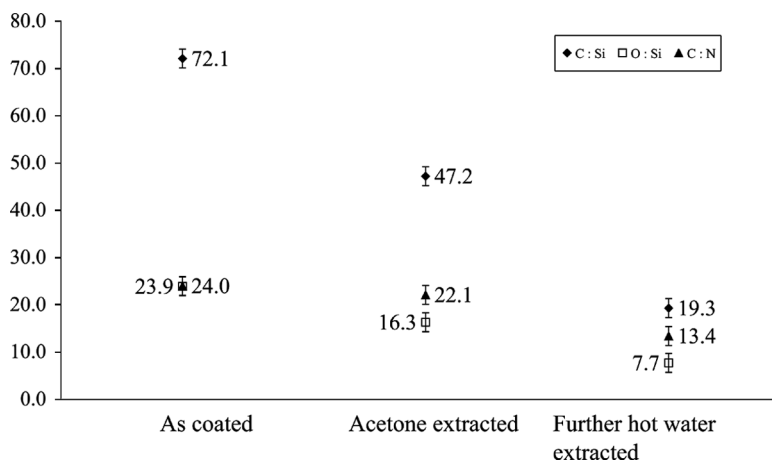

FIGURE 5 Plot of C : Si, O : Si, C : N ratios for PU and APS coated, acetone extracted, and further hot water extracted chopped E-glass fibres.

was extracted, because the exposed layer would contain a high percentage of APS which has a low $C:N$ ratio. After hot water extraction, the $C:N$ ratio is further reduced indicating that the concentration of APS in the residue was increased. This could be attributed to the hydrolysis of the PU which seems unlikely. However, it is known that hot water extraction of a APS deposit occurs through hydrolysis of the siloxane bonds [16,17,20] so that the most likely explanation for the release of PU is that an interpenetrating network had formed.

4. DISCUSSION

4.1. The Structure of Hydrolysed Silane Deposit

The binding energy assignments of N 1s for 1% APS coated E-glass before and after water extraction (Fig. 3) are in good agreement with those reported by Horner *et al.* [21], in a high resolution study of hydrolysed APS (HAPS) deposited on a range of metal substrates, and with other literature reports [22–24]. A possible explanation for the formation of protonated amino groups on the E-glass surface is that the amine is protonated by the hydroxyl groups $(-OH)$ present in the siloxane layer as well as on the glass surface. The presence of a significant number of hydroxyls on the unsilanised glass surface has been confirmed by the ToF-SIMS studies of Wang and Jones [25]; the density of hydroxyl groups has also been calculated by the maximum value of contact angle to water in octane at the point of zero charge [15,26].

In addition, the fraction of free amino groups $(-\underline{N}H_2)$ from APS coated E-glass fibres decreases to approximately 40% after warm and hot water extractions (Table 4), which is accompanied by a decrease in the nitrogen concentration (Table 3). Thus, the free amine concentration decreases with the removal of the physically adsorbed APS deposits. The exposed layer after hot water extraction is considered to be the crosslinked APS layer [2]. Therefore, the crosslinked APS deposit would appear to have less free amino groups than the physically adsorbed APS deposit. In other words, the amino groups are densely protonated in the crosslinked APS deposit close to the glass surface. This could be attributed to the interaction between amino groups $(-\underline{N}H_2)$ of APS silane molecules and the hydroxyl groups $(-OH)$ at the glass surface, and/or the interaction between amino groups $(-\underline{N}H_2)$ of the APS silane layer firstly adsorbed onto the glass surface and the hydroxyl groups $(-OH)$ of the subsequent

APS silane layer deposited afterwards. Specific interactions cannot be uniquely determined with XPS analysis.

Previous work [5,6,25,27] has indicated that silanes with an amino group have a tendency to deposit from aqueous solutions onto the glass surface in two orientations. One was proposed by Chiang and Koenig [27], where the glass surface silanols condense with the hydrolysed silane. The other was caused by the reaction between the amino group of the silane and the silanol groups on the glass surface. The degree of silanation and the orientation of silane molecules on the glass surface can be affected by the glass substrate, the pH of the silane solution, and the concentration of silane solution.

Since the outer surface of the APS deposit is rich in free amines, which are available for further interaction as they are expected to be orientated outwards, then it would follow that a good adhesive bond between a resin matrix and the silanised glass can be expected when APS is used as the coupling agent.

Table 3 shows the changes in N concentration and the N : Si ratio of the 1% APS coated E-glass fibres before and after water extraction. It is assumed that the warm water extraction removes the oligomeric component of the APS deposit on E-glass fibres. The further slight decrease in the nitrogen concentration after hot water extraction indicates the presence of an "intermediate component" which is often referred to as weakly chemisorbed. Wang *et al.* [20] have associated this with a hydrolysable network chain component because the molecular size of the fragments in the ToF-SIMS spectrum was reduced significantly. The component revealed by hot water extraction is a crosslinked siloxane network, with a high percentage of protonated amine. Thus, the above arguments can be used to describe the silane deposit on an E-glass substrate schematically in Fig. 6a. The long linear polymeric network ends have been omitted for clarity.

The AFM images observed on the 1% APS coated E-glass fibres in Fig. 4 seem to confirm the structure of the APS deposit on an E-glass fibre surface. The hills observed in Fig. 4a are considered to be associated with the APS deposit on E-glass fibres. The density and distribution of these hills were modified by warm water treatment. The microstructure of the chemisorbed component in the APS deposit is imaged in Fig. 4b. After further hot water extraction, pits appear as shown in Fig. 4c that may result from the hydrolytic removal of the randomly coiled chains at the ends of the crosslinked network in the chemisorbed component APS.

Therefore, the APS deposit on E-glass fibres appears to have three components. One component is composed of physisorbed, warm water soluble oligomers with high fraction (64%) of free amino groups. The

intermediate layer, which is often referred to as the weakly chemisorbed component, consists of a crosslinked siloxane polymer with long chain network-ends. 60% of amine groups are in the protonated form. Since the latter does not change on hot water extraction, it can be inferred that the so-called strongly chemisorbed component mostly consists of the cross linked deposit, without the presence of long network-ends. The hydrolytic resistance of the network is higher because of the statistical need to break more chemical bonds. It has been reported previously [15,16] that the glass network modifiers such as Al can be concentrated at the surface of silane treated E-glass fibres. The incorporation of these elements into the siloxane network may also contribute to its hydrolytic resistance.

4.2. Structure of Silane Containing Size

The XPS data in Table 5 have been interpreted by analysing the change in elemental ratios after extraction with acetone and hot water. As seen in Fig. 5, the C : Si ratio decreases steadily. According to the arguments presented by Thomason [19] and Thomason and Dwight [18], this demonstrates that the sizing polymer was partially extracted by acetone. Since C : N ratio remains effectively constant after acetone extraction, both the silane and PU components are removed. However, after further extraction with hot water, both the C : Si and C : N ratios decrease. This confirms that soluble silane oligomers as well as network siloxane exists within the sizing deposit. Furthermore, if we assume that the PU is hydrolytically resistant to hot water, then its removal in hot water can only be explained by the formation of an interpenetrating network which releases the PU when the siloxane bonds hydrolyse. Thus, a semi-interpenetrating network (semi-IPN) between the poly-HAPS and the PU film formers can form during the coating process.

It is generally accepted that the silane is partitioned at the glass surface [28]. The film former in the sizing can diffuse to differing degrees into the matrix during fabrication of the composite [28]. In addition, the oligomeric component in the silane deposit will also diffuse into the matrix [2]. Figure 6 gives a schematic of the formation of the glass/sizing/matrix interphase, which is represented as a bonded semi-IPN. Figure 6a illustrates the structure of the hydrolysed APS deposited onto an E-glass fibre surface showing a 3-D polysilane network containing oligomeric silanes. The latter are shown displaced for simplicity. Therefore, when the silane is codeposited with a polymeric film former or size, as shown in Fig. 6b, an IPN between the 3-D network silane and the linear polymer film former (PU) exists.
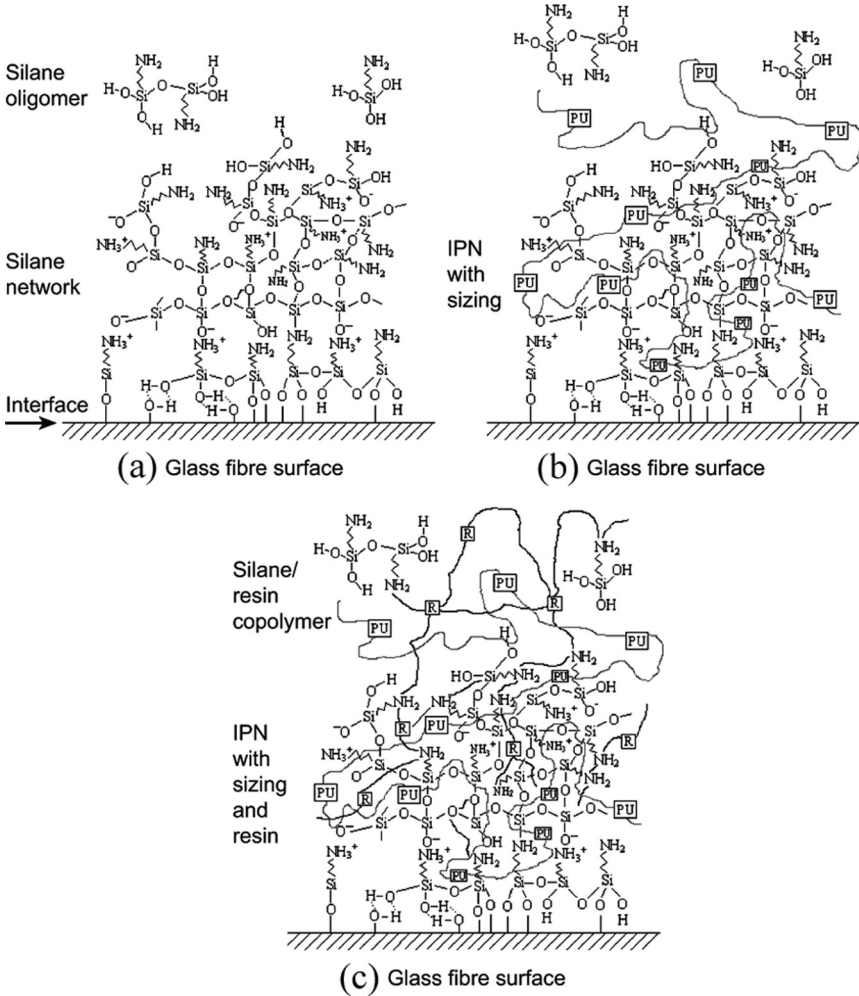
FIGURE 6 Schematic of composite interface between glass fibre, sizing, and matrix. (a) Chemical structure of hydrolysed APS on glass fibres, (b) IPN between hydrolysed APS and the PU film polymer or sizing, (c) Interphase in a glass fibre composite where a reacted IPN between network silane, film former, and resin matrix (R) forms.

The oligomeric component may be present in the body of the deposit or as a surface active agent adsorbed onto the polymer film former. When the fibres are impregnated with a resin (R), the mobile silane oligomeric component of the sizing will diffuse into it, to varying degrees, leaving molecularly sized voids which will accept the resin molecules.

The compatibility of the polymeric film former with the resin will also determine the degree of swelling of the deposit and eventual reptation of the film former polymer into the resin, which will eventually become the matrix. Figure 6c illustrates the structure of the interphase in a composite which consists of an IPN between the matrix, film former, and silane network and extends over a length scale of several molecular layers. The degree of film former diffusion depends on the thermodynamic compatibility and molecular weight of the components [2]. The role of the chemisorbed APS is to provide a mechanism for the formation of molecularly sized pores, into which the resin molecules can diffuse to form a semi-IPN which promotes adhesion through molecular interlocking. Thus APS can act as an adhesion promoter for a range of matrix polymers independent of chemical coupling. For reactive systems a bonded IPN can form as shown in Fig. 6c.

5. CONCLUSIONS

Both the APS and sizing (containing APS and PU) deposits on E-glass fibre surface have been investigated. The presence of components of differing hydrolytic stability in the APS deposit has been confirmed by extraction treatments, which are associated with physisorbed, loosely chemisorbed, and strongly chemisorbed components. Amino groups have been found to be partially protonated by the hydroxyl groups present in the siloxane layer and on the glass surface. More protonated amine groups have been found in the strongly chemisorbed component compared with the physisorbed and loosely chemisorbed components. The AFM images show the difference in topography of the APS coating before and after water extraction.

The soluble components of the sizing on fibres will diffuse into the matrix to a varying degree. In effect, the chemisorbed silane can accept the matrix molecules. This structure is considered to be that of an IPN with a linear thermoplastic or a semi-IPN in the case of a thermosetting resin. The thermomechanical properties of the interphase which forms has a major influence on fibre composite performance.

ACKNOWLEDGMENTS

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