AN XPS STUDY OF ORGANOSILANE AND SIZING ADSORPTION ON E-GLASS FIBRE SURFACE

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Abstract

   Organosilanes are often used in commercial sizings to provide increased compatibility of fibres and promote adhesion between glass fibre surfaces and the resin in the glass fibre reinforced polymer composite. The modification of fibre surface with silane and sizing is important to provide composites with the best properties. Therefore, it is necessary to understand the interaction of organosilanes and sizings with glass surfaces better.

   X-ray photoelectron spectroscopy (XPS) was used to investigate γ-aminopropyltriethoxysilane (APS) and a simple sizing system containing polyurethane (PU) and APS adsorption on E-glass fibre surface. It has been found that both APS and sizing (containing APS and PU) deposits on E-glass fibre surface contained components of differing hydrolytic stability. This structure of APS deposit was considered to be semi-interpenetrating network.

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].

   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 promote the adhesion between glass fibre surfaces and the matrix in a glass fibre reinforced polymer composite [3]. They can displace adsorbed water on the glass fibre surface; create a surface of the correct thermodynamic characteristics for complete wetting by the resin and develop strong interfacial bonds between the fibre and resin [2].

   Since the 1960s [4], Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), XPS and secondary ion mass spectrometry (SIMS) have been extensively used 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].

   In this paper, APS was employed because of its wide ranging applications as well as the presence of a nitrogen atom which enables a detailed surface analysis for XPS. Warm water and hot water extractions were employed to investigate the components of differing hydrolytic stability at the silane-glass interface. A simple sizing system containing 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 with the structure of NH_2-$(CH_2)_3$-Si-$(OC_2H_5)_3$ (GE Speciality Materials, Meyrin, Belgium) was used for silanising unsized E-glass fibres (Owens-Corning, Granville, USA). APS was hydrolytically dissolved in deionised water at a concentration of 1% by weight. E-glass fibres were immersed in 1% APS solution for 15 minutes at room temperature. After silanisation, glass fibres

were dried in a desiccator to let the water evaporate at room temperature. Then they were cured at 100 °C for 2 hours in an oven. They are referred to as APS coated samples.

Some of the APS coated fibres were extracted in deionised water at 50 °C for 24 hours in an oven and dried in a vacuum oven at 50 °C to remove the physisorbed silane layer. These samples are called warm water extracted samples. Some of them were further extracted in hot water at 100 °C for another two hours to remove loosely chemisorbed silanes and then dried in a vacuum oven at 50 °C. They are known as hot water extracted samples.

Chopped E-glass fibres sized with APS and polyurethane (PU) (Owens-Corning, Granville, USA) were also investigated in this study. Acetone extraction was performed at room temperature for 24 hours to remove PU in order to study the interaction of APS with E-glass fibre surface. Then they were washed with deionised water for 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 another two hours to remove physisorbed and loosely chemisorbed silane layers and then dried in a vacuum oven 50 °C. They are referred as hot water extracted chopped fibres.

2.2 XPS Analysis

XPS was carried out using Kratos AXIS ULTRA at the University of Sheffield. 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 FAT (fixed analyser transmission) mode, with a pass energy of 160 eV for wide scans and a pass energy 40 eV for high resolution scans. 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.

3 Results and Discussions

3.1 Control E-glass Fibre

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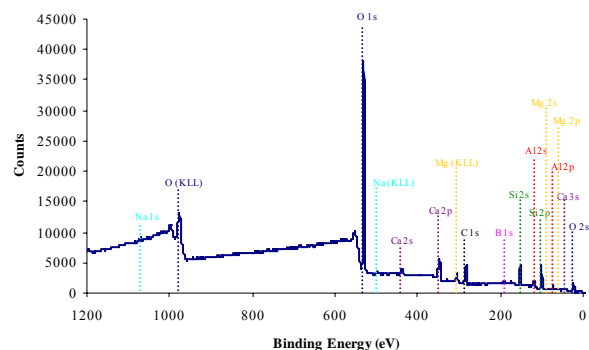

Fig. 1. XPS wide scan spectrum of control E-glass fibres.

Tab. 1. Atomic concentrations of control E-glass fibres determined from the wide scan spectrum.

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

The carbon signal, which appears at the binding energy of about 285 eV in the spectrum, results from carbon contamination during fibre production and subsequent sample preparation. The atomic concentration of carbon decreased with take-off angles. It is 67 % of C-C/H, 20 % of C-O-C/H, 5 % of C=O/O-C-O and 8 % of O-C=O ester/carboxylic acid species according to the high resolution C 1s curve fitting.

E-glass fibre surface and bulk compositions are shown in Tab. 2. For comparison with the bulk composition data obtained by XRF (done by D. Norga and V. Kempenaer in Battice European Testing Lab), the carbon contamination from XPS surface analysis and the oxygen associated with carbon (O_C) were ignored.

The concentrations of calcium and magnesium are lower on the surface than in the bulk of E-glass fibres, however, aluminium concentration is slightly higher on the E-glass fibre surface.

Tab.2. A comparison of the relative atomic compositions of E-glass fibre surface and bulk.

| Element | Atomic composition of E-glass Fibre (%) | |
	Surface Analysis[†]	Bulk Analysis[*]
Si	20.2	18.9
O	63.7	61.9
Ca	4.9	6.5
Al	6.2	6.0
Mg	0.8	2.2
Na	0.5	0.3
B	3.7	4.1

[*]Bulk Analysis from D. Norga and V. Kempenaer (Battice European Testing Lab using X-Ray Fluorescence). [†]Surface Analysis ignored C contamination.

3.2 APS Coated E-glass Fibre

A typical wide scan spectrum at a take-off angle of 45° from 1% APS coated E-glass fibres is shown in Fig. 2. The appearance of N 1s at the binding energy of ~ 400 eV confirms the deposit of APS on E-glass fibres. High resolution N 1s is fitted with two components associated with free amino groups ($-NH_2$) at a binding energy of 399.6 eV and protonated amino groups ($-NH_3^+$) at a binding energy of 401.4 eV (Fig. 3).

Similar curve fitting has also been reported by Horner et al [10], in a high resolution XPS study of hydrolysed APS deposited on a range of metal substrates, and with other literature reports [11-13]. The formation of protonated amino groups on E-glass fibres is caused by the protonation of amino groups in APS by the hydroxyl groups (-OH) present in the siloxane layer as well as on the glass surface. The presence of hydroxyl groups on unsilanised glass surface has been confirmed by the ToF-SIMS studies of Wang et al. [14].

Previous work [5-6, 15] has already indicated that silanes with an amino group have a tendency to deposit onto the glass surface in two ways from aqueous solutions. One was proposed by Chiang and Koenig [15], 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 glass surface can be affected by glass substrate, pH of silane solution, concentration of silane solution, etc.
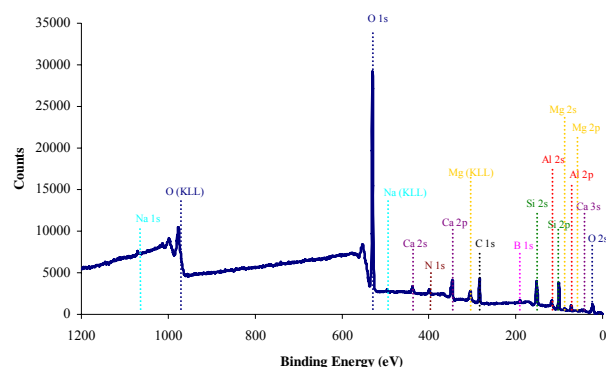

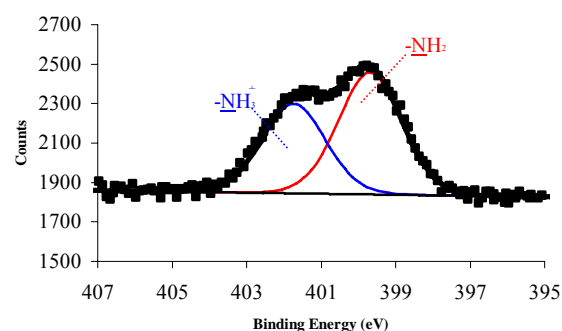Fig. 2. XPS wide scan spectrum of 1% APS coated E-glass fibres.

Fig. 3. Curve fitting of N 1s from 1% APS coated E-glass fibres.

The atomic concentrations of elements from 1% APS coated, warm water extracted and hot water extracted E-glass fibre surfaces are given in Tab. 3., which are obtained from the quantification of XPS wide scan spectra at a take-off angle of 45°. The thickness of the APS deposit on E-glass fibres is less than the analysis depth of XPS because the N : Si ratio is lower than 1 for hydrolysed APS.

After warm water extraction and further hot water extraction, the concentration of nitrogen from APS deposit decreased gradually from 2.5% to 2.3 % and 2.0 % respectively. The N : Si ratio was reduced from 0.16 to 0.14 after warm water extraction and to 0.12 after hot water extraction. Meanwhile, the concentrations of Ca and Al from the E-glass fibre substrate increase. It shows that part of the APS deposit has been extracted and more of the glass substrate has been exposed. The Al concentration increases to 5.1% after hot water extraction, which is very similar to or even higher than 5.0% of Al from control E-glass fibre surface.

Tab. 3. Comparison of surface composition of 1% APS coated and water extracted E-glass fibres determined from wide scan spectra.

Element	Atomic concentration of surface elements (%)		
	APS coated	Warm water extracted	Hot water extracted
C	21.8	20.6	19.3
Si	16.0	16.1	16.5
O	50.7	50.9	51.3
Ca	2.3	2.5	2.6
Al	4.7	4.8	5.1
Mg	0.6	0.9	1.1
B	1.4	1.9	2.1
N	2.5	2.3	2.0
N : Si	0.16	0.14	0.12

Warm water extraction also leads to an increase in the intensity of protonated amino groups ($-NH_3^+$) on 1% APS coated E-glass fibres (Tab. 4.). However, hot water extraction did not change the fractions of free amine in the peak N 1s.

It is assumed that the warm water extraction removes the oligomeric component of the APS deposit on E-glass fibres. The nitrogen functionalities in the physically adsorbed component are mainly free amino groups, which decrease after the extraction with warm water. The further decrease in the nitrogen concentration by hot water extraction indicates the presence of an 'intermediate component' in the APS deposit on E-glass fibres. It is considered to be weakly chemisorbed APS. Wang et al. [16] have associated this with a hydrolysable network chain component. The molecular size of the fragments in the ToF-SIMS experiment was reduced significantly. The component revealed by hot water extraction is a crosslinked siloxane network, with a higher percentage of protonated amine. This can explain the changes in nitrogen concentration (Tab. 3.) and intensity of protonated amine (Tab. 4.) for 1% APS coated E-glass fibres with water extractions.

Therefore, the APS deposit on E-glass fibres appears to have three components. One component is composed of physisorbed, warm water soluble oligomers with higher percentage of free amino groups. Hot water soluble component forms the intermediate layer, which is weakly chemisorbed. Wang et al. [16] concluded using ToF-SIMS that it was the linear ends of the network which were hydrolytically extractable in hot water. The crosslinked APS deposit was strongly chemisorbed

onto the E-glass fibre surface and contained a higher percentage of protonated amino groups.

Tab. 4. Comparison of N 1s core line analysis for 1% APS coated and water extracted E-glass fibres.

	$-NH_2$ (%)	$-NH_3^+$ (%)
APS coated E-glass fibres	58	42
Warm water extracted	40	60
Hot water extracted	40	60

3.3 Sizing (PU and APS) Coated E-glass Fibre

The chopped E-glass fibres with a full sizing (PU and APS) have been also investigated by XPS with the assistance of a model based on a patchy sizing overlayer hypothesis [17]. Acetone extraction was performed, which is expected to remove the PU component and the physisorbed APS in the sizing. Further hot water extraction is expected to remove the loosely chemisorbed APS layer and expose the 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 extractions are compared in Tab. 5. Thomason [18] has 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 [17]. It can be seen from Tab. 5. and Fig. 4. that the C : Si ratios for the chopped E-glass fibres are mostly an excess of 10, which suggests the XPS data is dominated by the sizing deposit.

Tab. 5. Comparison of XPS data from sizing coated, acetone extracted and further hot water extracted chopped E-glass fibres.

	Sizing coated chopped E-glass fibres		
	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

Fig. 4. 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. The decreases in C : Si and O : Si ratios after acetone and hot water extraction suggest that the polyurethane in the sizing deposit has been partially removed. The ratio of C : N is reduced 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 signals are considered to arise mainly from APS in the sizing. Thus, the slight decrease in C : N ratio indicates that acetone extracts not only polyurethane but also some low molecular weight APS oligomers. Otherwise, the C : N ratio would decrease significantly because the exposed layer contains a higher percentage of APS with lower C : N ratio. Further hot water extraction reduces the C : N ratio as a result of higher percentage of APS contributing to XPS signals. This is in an agreement with the results shown in Section 3.2 on APS coated E-glass fibres. The APS deposit on E-glass fibres contains oligomers, crosslinked network and the linear ends of the network. A semi-interpenetrating network (semi-IPN) structure will form with the polyurethane, which gives these extraction results.
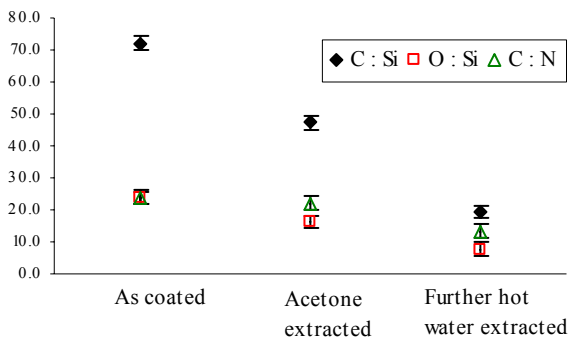

Fig.4. Plot of C:Si, O:Si, C:N ratios for PU and APS coated, acetone extracted and further hot water extracted chopped E-glass fibres.

It is generally accepted that the silane is partitioned at the glass surface [19]. The film former in the sizing can diffuse to differing degrees into the matrix during fabrication of the composite [19]. In addition, the oligomeric component in the silane can diffuse into the matrix as well because it is mobile [2]. Jones [20] has shown a schematic diagram of glass/sizing/matrix interphase, which is represented as a bonded semi-interpenetrating network (Fig. 5.). It shows that the soluble components of the sizing on glass fibre will diffuse into the matrix to a varying degree when the glass fibres are embedded in a matrix. The degree of sizing diffusion depends on

the thermodynamic compatibility of the 'blend' and also the rate of diffusion is a function of molecular weight of each component [2].
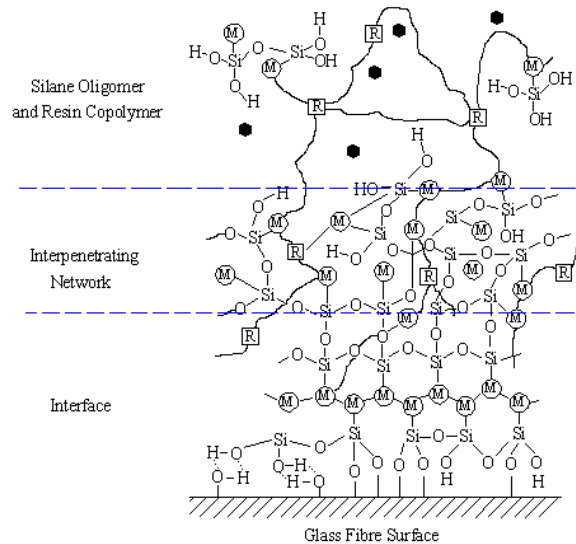

Fig. 5. Schematic of composite interface between glass fibre, γ-methacryloxypropyl-trimethoxysilane and matrix. M is methacryloxypropyl group in γ-methacryloxypropyl-triethoxysilane; R is resin matrix; ⬢ is dissolved binder and/or size [20].

Since the oligomeric APS component, in the sizing containing PU and APS on chopped E-glass fibres, is mobile, it can diffuse into a matrix during composite processing. As a consequence, the chemisorbed APS will be like a molecular sponge with molecular pores, which can accept the resin molecules. This kind of semi-interpenetrating network will aid adhesion.

4 Conclusions

Both the APS and sizing (containing APS and PU) deposits on E-glass fibre surface have been investigated by XPS. The presence of components of differing hydrolytic stability in both deposits has been confirmed. 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 a semi-interpenetrating network and have an influence on the composite properties.

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