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ORIGINAL CONTRIBUTION

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Deposition characteristics of γ-ureidopropyltrimethoxysilane onto E-glass fibres using toluene and carbon tetrachloride as carrier solvents

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Abstract Industrial grade γ-ureidopropyltrimethoxysilane was adsorbed onto industrial grade E-glass fibres from toluene and carbon tetrachloride at 23 °C. The treated surfaces were characterised using thermogravimetry, diffuse reflectance Fourier transform IR spectroscopy, electron spectroscopy for chemical analysis, scanning electron microscopy and the zeta potential. When ureidosilane was deposited from toluene and CCl_4, both of which have very low hydrogen-bonding ability, a ureido surface was obtained. The ureidosilane deposited from CCl_4 hydrolysed at the surface and condensed to form a solvent-swollen Si–O–Si network. The ureidosilane deposited from toluene also hydrolysed at the E-glass surface. Condensation of the silane deposited from toluene was not apparent. Aluminium dissolved from the E-glass surface was condensed into the network of the silane deposited from CCl_4. Aluminium was not detected at the surface of the samples with ureidosilane deposited from toluene.

Key words Silane · Siloxane · E-glass · Electron spectroscopy for chemical analysis · Zeta potential

Introduction

Plueddemann [1] suggested that when exposed to moisture, glass-reinforced plastics (GRP) were susceptible to failure at the glass/polymer interface if no chemical bond existed between the glass surface and the polymer. By using a silane coupling agent which was chemisorbed onto the glass surface, and would then react chemically with the polymer network, a much stronger composite was produced [1]. The improved strength conferred by silanes has been demonstrated in GRP composites by other workers [2, 3, 4].

Previously we reported that by using ethanol, a solvent with high hydrogen-bonding and polarity potentials, a ureidosilane could be induced to deposit with the amino groups uppermost [5]. Later results indicate that whilst the silane was most likely deposited the "right way up" at the glass surface, the outer layers were deposited "upside down" owing to the formation of a "hemi-micelle-like" structure, which resulted in an Si–O–Si surface [6]. A silane containing amino groups was as likely to bond with the amino group to the glass surface as with the hydrolysed silanol group to the surface [7, 8]. It was proposed that when γ-aminopropyltrimethoxysilane was deposited from dilute solutions, it was laid flat on the E-glass fibre, with both the alkoxy and amine functions binding to the surface. Moreover, as the concentration increased the molecules were "forced" to stand upright, resulting in an increasingly basic surface [9, 10]. Two layers of silane were proposed: a thin chemisorbed layer of a few angstroms and a much thicker physisorbed layer [7, 11, 12]. The latter layer was easily removed by use of a series of washing solvents [11, 12].

Industrially silanes are applied as previously hydrolysed aqueous solutions [1, 13]. Silanes in such solutions are hydrolysed and condense to form siloxane oligomers, the molecular weight of which is dependent upon the pH of the deposition solution [1, 13]. When silanes are deposited from dry organic systems, the layers of hydrogen-bonded water adsorbed onto the surface of E-glass fibres would be sufficient to drive the hydrolysis and condensation reactions [14, 15].

Industrial E-glass fibres and ureidosilane have been used with dry organic solvents to examine the deposition behaviour of alkoxysilane monomers. Characterisation of the deposited surfaces is expected to reveal whether there is sufficient water adsorbed onto the surface of E-glass fibres to hydrolyse and condense monomers deposited from dry solutions. Additionally the behaviour of ureidosilane monomers in a range of solvents has been characterised [5, 16].

When deposited from aqueous solutions between pH 4 and 10 onto E-glass fibres ureidosilanes deposited "upside down" [6]. Thus, a range of organic carrier solvents has been used to examine the conditions required for "right-way-up" deposition and to determine if hydrolysis and condensation would occur at the E-glass fibre surface [5, 16].

Solubility parameter

According to the theories proposed by Hansen, Hoftyzer and van Krevelen, in order for the silane to remain dissolved, the difference between the solubility parameters of the solvent and the silane should be no greater than 2 $MPa^{1/2}$ [17, 18, 19]. Plueddemann [1] suggested that in solvents of dissimilar solubility parameter the silane formed micellelike structures.

The contributions from δ_h, δ_p and δ_d, which relate to the hydrogen bonding, polar forces and dispersion forces, respectively, can be determined separately. These may then be used to produce a total, δ_t, which is the solubility parameter of a material [19]. The solvents used in the wash sequence had increasing hydrogen-bonding ability as described by the δ_h portion of the solubility parameter [18, 19].

Experimental

A sequential solvent wash procedure with γ-ureidopropyltrimethoxysilane (ureidosilane) deposited from toluene and from CCl_4 was investigated. The solubility parameter (δ_t) of both the deposition solvent and the washing solvents, in relation to the silane in its unhydrolysed, partially hydrolysed and fully hydrolysed forms, is believed to be significant in determining the adsorption of the silane onto the E-glass fibre surface [5, 16] (Table 1). Other relevant factors were thought to be the ability of the solvent to interfere with the condensation reaction, the solubility of leached aluminium into the siloxane layer and the silane concentration.

Materials

Chopped E-glass fibres, diameter 11.0×10^{-6} m, length 1.0×10^{-3} m, were kindly supplied by Ahlström Glass Fibre (Karhula, Finland). Toluene (AnalaR 99.5%, bottled) was purchased from BDH, carbon tetrachloride (AR grade) (purity greater than 99%) was obtained from Baker, dichloromethane (99.6% ACS grade) stabilised with 0.2% ethanol, acetone (100% technical grade), tetrahydrofuran (THF, 99% ACS reagent), which was stored under dry nitrogen after opening to prevent oxidation and methanol (99.8% GPR grade) were obtained from Aldrich and were used without further purification. The water content of all the solvents was checked by the Karl Fischer method and was determined to be less than 50 μl/l solvent. γ-Ureidopropyltrimethoxysilane was kindly donated by Aspokem Oy, Finland (Fig. 1).

Methods

Solutions of ureidosilane (200 ml of 2% by weight) were prepared in toluene and CCl_4. To these solutions, 30 g E-glass fibres was

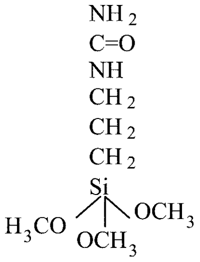


Fig. 1 Structure of γ-ureidopropyltrimethoxysilane

Table 1 Solubility parameters for organic solvents used: unhydrolysed, partly hydrolysed and fully hydrolysed γ-ureidopropyltrimethoxysilane

Solubility parameters	δ_t ($MPa^{1/2}$)	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)
Carbon tetrachloride [14] (CCl_4)	17.7	17.7	0	0
Toluene [14]	18.3	16.4	8	1.6
Dichloromethane [14]	20.3	18.2	6.3	6.1
Acetone [14]	20.0	15.5	10.4	7.0
Tetrahydrofuran [14] (THF)	19.4	16.8	5.7	8.0
Methanol [14]	29.6	15.1	12.3	22.3
Silane Y11542 unhydrolysed	20.3	15.6	7.3	10.7
Silane Y11542 1 $-OCH_3$ hydrolysed	23.8	16.3	7.2	15.8
Silane Y11542 2 $-OCH_3$ hydrolysed	28.7	17.3	9.3	20.9
Silane Y11542 3 $-OCH_3$ hydrolysed	35.7	18.7	14.6	26.6

added and the solutions were sealed and gently agitated at 23 ± 2 °C for 16 h. The E-glass fibres were then removed and washed with either toluene or CCl_4. The sample was "flash dried" at 120 °C for 5 min and the washing procedure was repeated a further two times. The E-glass fibres were then dried for 3 h at 120 °C. The samples were designated the toluene- or CCl_4-washed sample respectively. Approximately 6 g E-glass fibres was removed and stored. The remaining sample was subjected to a sequential washing procedure of three washes per solvent, with "flash drying" between each washing cycle and a final drying at 120 °C for 3 h. A 6-g sample of the treated E-glass fibres was removed and stored after each washing and drying cycle. The sequence of solvents used was dichloromethane, acetone, THF and methanol.

The samples were analysed using a Netzsch TG 290, using a programme with a 20-min isothermal period to stabilise the samples, followed by a temperature ramp to 550 °C (10 °C/min), followed by a second 20-min isothermal period. Nitrogen at a flow rate of 15 ml/min was used as the protective and the carrier gas.

Elemental scanning was accomplished with a Perkin Elmer ESCA PHI 5400, using a 45° takeoff angle and an Mg Kα source which generated X-ray photoelectrons at 1,253.6 eV. A 1 mm-diameter molybdenum mask was used to maintain the orientation and "flatness" of the E-glass fibres; this prevented any shadowing by raised E-glass fibres. The sample had a tendency to "charge up" during the electron spectroscopy for chemical analysis (ESCA): to account for these effects all the data obtained were corrected to an internal standard of the binding energy of C1*s* at 284.6 eV [7, 12].

Diffuse reflectance Fourier transform (DRIFT) spectra were recorded using a Bruker IFS 66 spectrophotometer. Background spectra were taken using dry potassium bromide powder. E-glass fibres were mounted parallel to the incident beam, as it was determined that spectra with minimum noise were obtained in this orientation. A spectrum of a clean E-glass fibre was subtracted from the spectra of the treated E-glass fibres.

The streaming (or zeta) potentials of the toluene and CCl_4 and the wash-sequence samples were measured using an Anton Paar electrokinetic analyser, described previously [6]. The surface charge of the E-glass fibres was low and so the Fairbrother–Mastin equation was used to calculate the streaming potential values.

Scanning electron micrographs were taken of all the samples, using a Cambridge Instruments Stereoscan 360.

A ^{29}Si NMR spectrum of ureidosilane was run in toluene on a Jeol 400 MHz nuclear magnetic spectrometer to determine if hydrolysis of the silane had occurred before use.

Results

^{1}H NMR confirmed that hydrolysis had not occurred in the ureidosilane/toluene sample; therefore, only a single silane species was present in the solution prior to deposition onto the E-glass fibres [20] (spectra not shown).

There was a high positive correlation between the binding energies of silica and oxygen; this was used to distinguish between a silicate and a silane surface [21]. Below 429.6 eV a silicate surface consistent with glass was indicated; between 429.8 and 430 eV a silane surface was suggested [21]. We propose that between 429.6 and 429.8 eV a patchy surface was implicit. Arora et al. [22] noted that peaks between 399.5 and 399.9 eV could be attributed to secondary amines and that nonprotonated primary amines may be seen at 399.0 ± 0.3 eV. Protonated primary amines were reported to be detected at a binding energy of 402 eV [23].

Treated E-glass fibres deposited from toluene and CCl_4 demonstrated weight losses between 2 and 7% of the total weight of the E-glass fibres (Fig. 2). The derivatives of the thermogravimetric analysis (TGA) traces showed two major weight losses for both sets of samples. The first minimum being between 200 and 240 °C and the second between 380 and 420 °C (Fig. 3). Under an inert atmosphere, desorption of the silane will occur. Loosely bound water desorbs up to a temperature of 120 °C.

The zeta potential measures the charge of the mobile ions associated with a surface; the isoelectric point (IEP) is the point at which the charge at this boundary equals zero. Titration of the ureidosilane in water using HNO_3 indicated that the pH = p*K*a balance point was 6.8; thus,

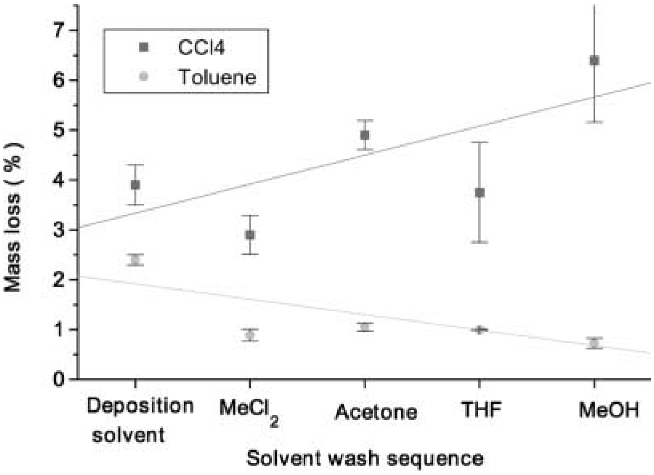


Fig. 2 Average mass loss change through the wash sequence of E-glass fibres treated with ureidosilane deposited from toluene and CCl_4

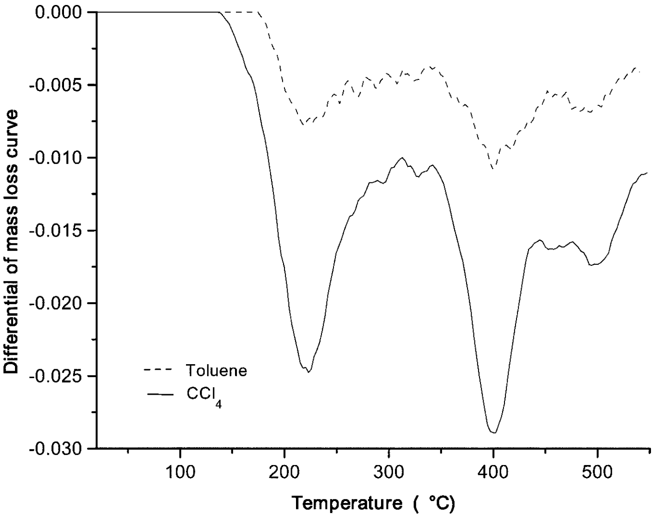


Fig. 3 Differentials of mass loss spectra of E-glass fibres with ureidosilane deposited from toluene and CCl_4

an IEP in the region of 6.8 would indicate a ureidosilane surface.

The zeta potential of the ureidosilane-treated E-glass fibres deposited from both toluene and CCl_4 decreased between electrolyte pH 8 and electrolyte pH 10. This denoted screening of the charges at the surface of the E-glass fibres, i.e., the adsorption of silane onto the E-glass surface.

The height of the peaks for primary amine (NH_2 at 3,210 cm^{-1}) and the methoxy shoulder (OCH_3 at 2,842 cm^{-1}) were divided by an internal standard, the height of the peak for methylsilane (–CH_2–Si at 2,940 cm^{-1}). The peaks at 3,110 and 3,210 cm^{-1} (stretching vibrations of secondary and primary amines, respectively) were detected throughout the washing sequence, confirming the presence of deposited silane. The peak at 2,842 cm^{-1} for the pure ureidosilane was shifted to 2,833 cm^{-1} when the silane was deposited onto the E-glass fibres. The shift was due to the Si group being attached to $(OCH_3)_3$ in the pure silane and to $Si(OH)_3$ on the E-glass surface.

Comparison of the peaks at 2,842 and at 3,210 cm^{-1} with that at 2,940 cm^{-1} gave ratios for amine and methoxy relative to total silane content. The ratio of the NH_2/CH_2Si was used to indicate removal of silane by washing, whilst the ratio of the OCH_3/NH_2 peak was used to indicate hydrolysis of the methoxy functional group to SiOH (Table 2).

Ureidosilane deposited from toluene

The amount of nitrogen on the surface of E-glass fibres treated with ureidosilane in toluene decreased owing to the removal of loosely physisorbed silane as the sample passed through the washing sequence (Table 3). This was further demonstrated by the reduction in the N/Si ratio with the washing sequence and the reduction in mass loss (Figs. 2, 4a, b).

Curve-fitting of the carbon spectra (ESCA) indicated that the amount of carbonyl (C = O) between 289 and 291 eV remained constant with respect to the total amount of carbon throughout the wash sequence (Fig. 5a). Correlation of the area under the C = O peak with the mass loss indicated that as the amount of C = O was reduced, as the samples passed through the washing sequence, the mass loss also decreased (Fig. 5b).

Aluminium was not detected on the surface of E-glass fibres treated with ureidosilane in toluene; this would confirm the silane surface detected using the O1*s*–Si2*p* ratio (Table 4).

For all the E-glass fibre samples treated with ureidosilane in toluene, peaks for N1*s* were seen between 399.4 and 399.8 eV. Curve-fitting indicated the presence of free nitrogen at 398.3 eV, hydrogen-bonded nitrogen at 399.6 eV and protonated nitrogen at 40 eV [6, 23]. The amount of free nitrogen increased as the sample passed through the solvent wash sequence (not shown).

Methoxy groups of the ureidosilane reacted with physisorbed water on the E-glass surface to form hydroxysilanes. The ratio of the shoulder at 2,842 cm^{-1} assigned to OCH_3 to the CH_2–Si peak (2,940 cm^{-1}) was very small for the samples which had been deposited from toluene. This indicated that almost all the $Si(OCH_3)_3$ had been hydrolysed to $Si(OH)_3$. DRIFT results indicated that more OCH_3 was removed than NH_2 from the E-glass fibres treated with ureidosilane in toluene (Fig. 6). This confirmed that OCH_3 was removed by both the washing procedure and by hydrolysis.

Correlation of the IEP with OCH_3 indicated that as the IEP was reduced with the washing sequence and the removal of ureido groups, so the intensity of the OCH_3 peak also reduced (Fig. 7).

Table 2 Ratios of diffuse reflectance Fourier transform spectra peak heights of NH_2/CH_2–Si and OCH_3/CH_2–Si. The spectra were of untreated E-glass fibres subtracted from γ-ureidopropyltrimethoxysilane-treated E-glass fibres. CH_2–Si was used as an internal silane standard

	Pure Y11542	Toluene	Dichloromethane	Acetone	Tetrahydrofuran	Methanol
NH_2/CH_2–Si	0.580	1.03	0.84	0.99	1.00	1.05
OCH_3/CH_2–Si	0.925	0.473	0.277	0.333	0.432	0.33
	Pure Y11542	CCl_4	Dichloromethane	Acetone	Tetrahydrofuran	Methanol
NH_2/CH_2–Si	0.578	1.57	1.68	0.47	0.62	0.51
OCH_3/CH_2–Si	0.928	0.567	0.576	0.450	0.518	0.443

Table 3 Concentration of elements (electron spectroscopy for chemical analysis, *ESCA*) detected on the surface of E-glass fibres treated with γ-ureidopropyltrimethoxysilane deposited from toluene

	Toluene	Dichloromethane	Acetone	Tetrahydrofuran	Methanol
O1*s*	21.84	26.14	27.32	26.21	28.77
C1*s*	58.52	53.28	47.68	56.87	55.11
N1*s*	12.31	12.44	15.26	10.07	9.39
Si2*p*	7.34	8.14	9.73	6.86	6.73

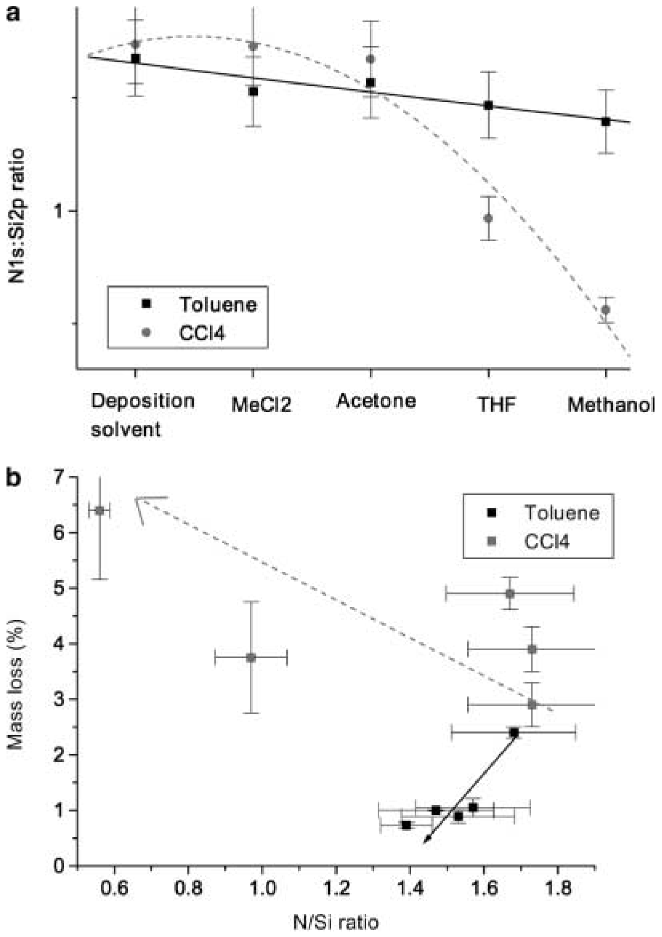


Fig. 4 **a** Change in the N1*s*/Si2*p* ratio (electron spectroscopy for chemical analysis, *ESCA*) with wash sequence for E-glass fibres treated with ureidosilane deposited from toluene and CCl_4. **b** N1*s*/Si2*p* ratios (ESCA) plotted against percentage mass loss of E-glass fibres treated with ureidosilane in toluene and CCl_4

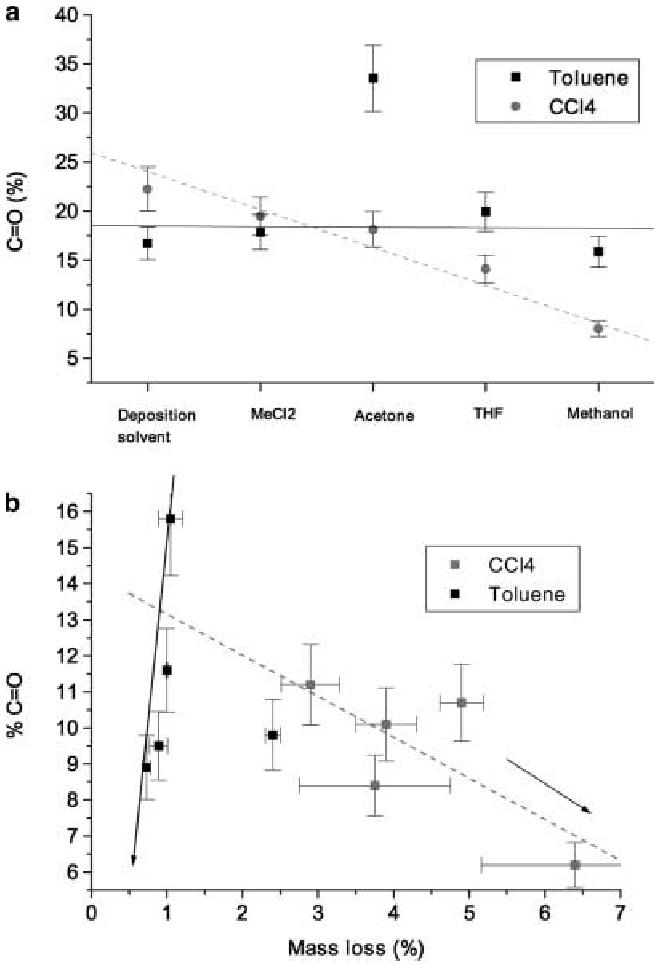


Fig. 5 **a** Change in the percentage C = O (ESCA) with wash sequence for E-glass fibres treated with ureidosilane deposited from toluene and CCl_4. **b** C = O (ESCA) plotted against percentage mass loss of E-glass fibres treated with ureidosilane in toluene and CCl_4

Comparison of the nitrogen to silica ratio (Fig. 4) with the IEP (Fig. 8, insert), demonstrated that the surface of the samples deposited from toluene, became more acidic as the amount of nitrogen at the surface decreased.

Ureidosilane deposited from carbon tetrachloride

The amount of ureidosilane deposited from CCl_4 was greater than that deposited from toluene despite the apparent similarity in the solubility parameters. The amount removed after each washing stage increased as opposed to the decrease expected, as measured by TGA (Fig. 2). The reduction in the N1*s*/Si2*p* ratio indicated that silane was removed at each washing stage (Fig. 4a). Protonated nitrogen (401.5–402 eV) indicated charged amino groups and a basic surface, as noted for a diaminosilane [6].

The binding energies for the nitrogen peak ranged from 399.6 to 399.8 eV, consistent with the presence of

Table 4 Difference in binding energies (ESCA) between O1*s* and Si2*p*, deposition solvent toluene

	Toluene	Dichloromethane	Acetone	Tetrahydrofuran	Methanol
O1*s*	532.4	532	532	531.9	531.9
Si2*p*	102.5	102.4	102.2	102.3	102.2
Difference	429.9	429.6	429.8	429.6	429.7
Surface	Silane	Patchy	Silane	Patchy	Patchy

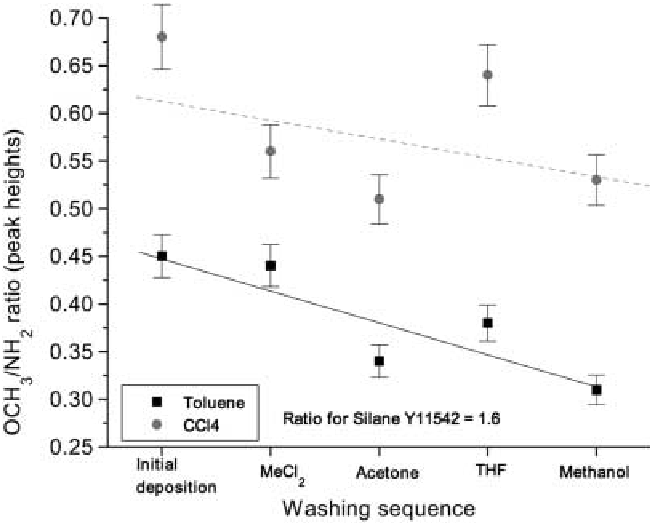


Fig. 6 Change in the OCH_3/NH_2 ratio of peak heights with wash sequence for E-glass fibres treated with ureidosilane deposited from toluene and CCl_4

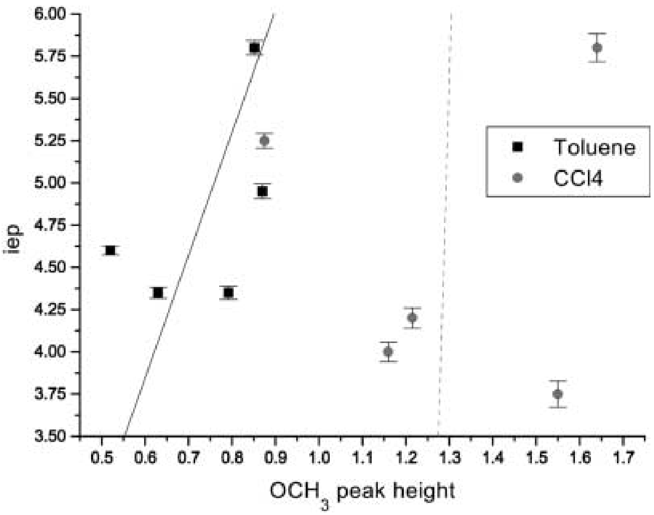


Fig. 7 Change in the isoelectric point (*IEP*) with wash sequence plotted against OCH_3 peak height for E-glass fibres treated with ureidosilane deposited from toluene and CCl_4

hydrogen-bonded nitrogen. Curve-fitting also indicated the presence of small amounts of free nitrogen, but no protonated nitrogen.

The ureidosilane in CCl_4-treated E-glass fibres became more acidic as the wash procedure progressed, with the exception of the methanol wash (Fig. 9 and insert). Methanol removed partially and fully hydrolysed silane and low-molecular-weight siloxane oligomers, revealing a ureido surface (Fig. 9). As the wash sequence of the sample deposited from CCl_4 progressed past the dichloromethane wash, the IEPs indicated a nonionic surface due to SiOH and Si–O–Si. The CCl_4 network was solvent-swollen and so was easily removed by further washes using solvents with δ_t and δ_h similar to that of the silane (acetone and THF).

The ratio of the OCH_3 (2,842 cm^{-1}) and NH_2 (3,210 cm^{-1}) peaks (DRIFT) confirmed that silane was removed from the surface by the washing procedure and that hydrolysis of the methoxysilane to hydroxysilane had occurred. A correlation between the reduced IEP and the reduced OCH_3 was noted, indicating that the ureido surface was associated with unhydrolysed silane; hence its ease of removal (Fig. 7).

Scanning electron microscope (SEM) photographs of E-glass fibres with silane deposited from both toluene (Fig. 10) and CCl_4 (Fig. 11) showed large amounts of silane deposited. Areas of excess silane deposition can be seen where E-glass fibres were glued together with silane and subsequently the silane bridge or "glue line" had broken. These "glue lines" would be vulnerable in the presence of, for example, solvents and mechanical stresses and strains. Deposition of large amounts of silane could be expected to be counterproductive to the enhancement of the physical and chemical properties of a GRP matrix.

Discussion

The first solvent wash with a solvent of higher δ_h (dichloromethane), especially in the sample deposited from toluene, resulted in the removal of non-condensed weakly physisorbed outer layers (TGA). This revealed a new outer layer with a higher percentage of cross-linked siloxane (zeta potential). As the samples passed through the washing sequence the increasingly strong hydrogen-bonding ability of the wash solvents interfered more with the hydrogen-bonded network. This resulted in larger amounts of physisorbed siloxane being removed.

Ureidosilane deposited from toluene

The ability of the solvents (TGA, DRIFT, and ESCA results) at each washing stage to remove silane after the repeated heating procedures indicated that an incompletely condensed siloxane surface which was not bound to the E-glass surface was present.

The ESCA results combined with an IEP of 5.95 demonstrated that after deposition and washing with toluene a surface due mainly to the ureido functional group was present.

Subsequent washing with non-inhibiting solvents allowed some condensation to take place and a siloxane surface, as measured by the zeta potential, was detected (Fig. 8, Fig. 8 insert). The wash with THF produced a

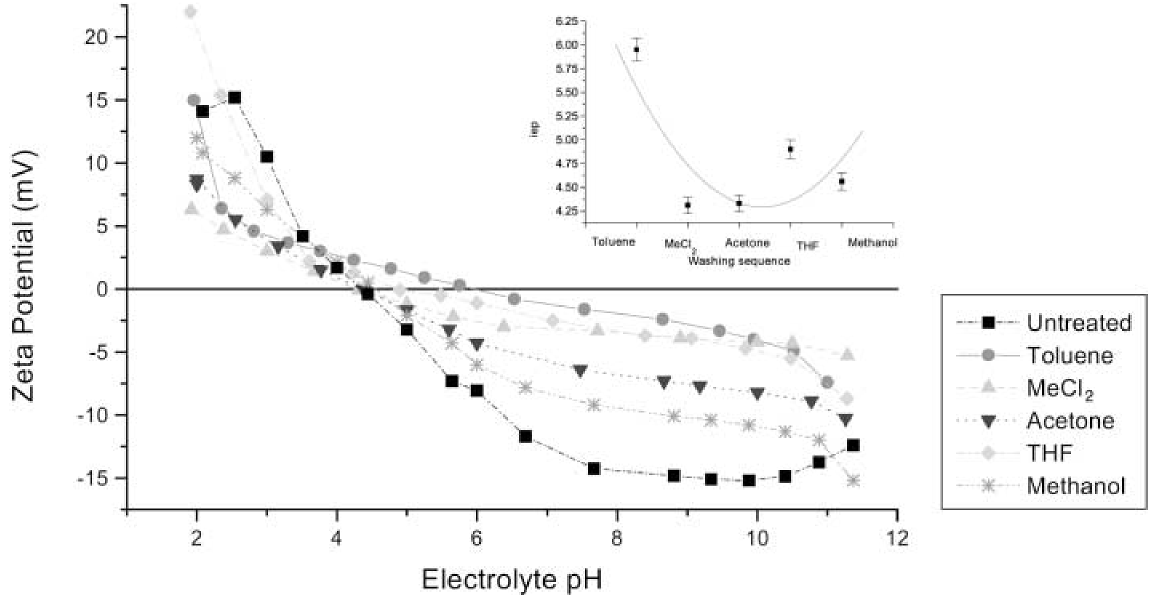


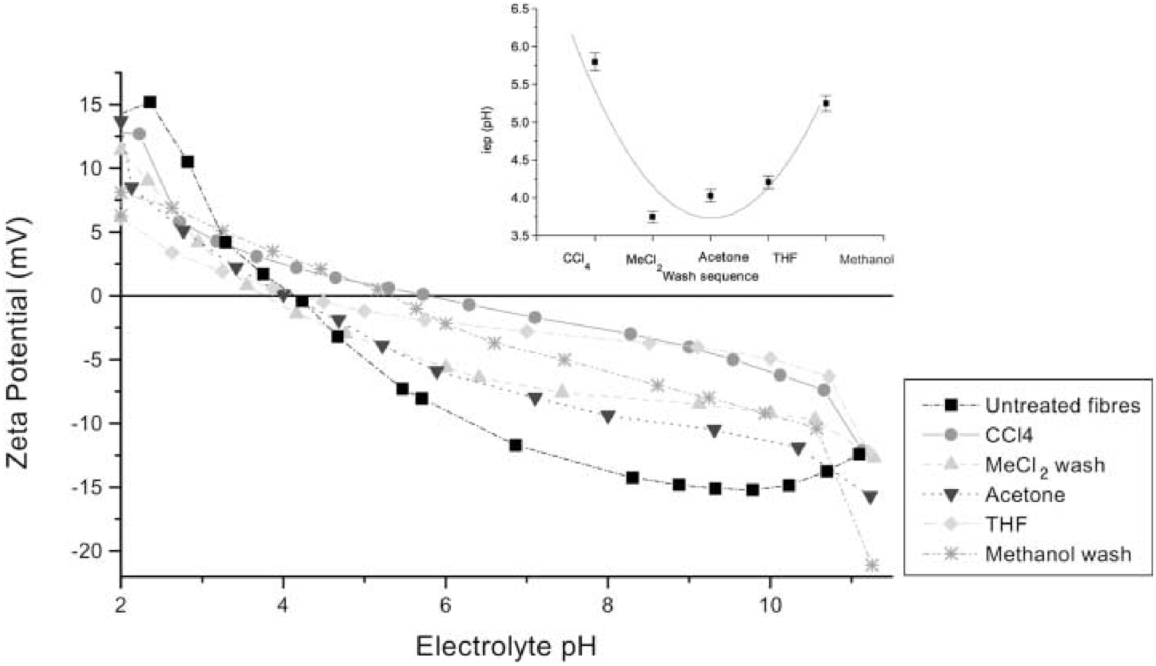
Fig. 8 Change in the zeta potential with wash sequence for E-glass fibres treated with ureidosilane deposited from toluene. *Insert* Change in the IEP with wash sequence for E-glass fibres treated with ureidosilane deposited from toluene

mixed orientation ureido/silanol surface; there is some indication that THF also inhibits the condensation reaction [17, 24].

The lack of aluminium on the surface of E-glass fibres treated with ureidosilane in toluene, confirms the silane surface indicated by the O1*s*/Si2*p* ratio. Additionally the absence of aluminium at the surface implied that condensation was minimal as aluminium has been detected as part of the condensed siloxane layer [6, 16]. The minimal condensation of silane could either result in poor physical and chemical properties of a GRP matrix or, if the polymer was able to bond into the silane forming a polymerised interphase, result in improved physical and chemical properties.

Ureidosilane deposited from toluene confirmed the trend of reduced mass loss with reduced C = O and

Fig. 9 Change in the zeta potential with wash sequence for E-glass fibres treated with ureidosilane deposited from CCl$_4$. *Insert* Change in the IEP with wash sequence for E-glass fibres treated with ureidosilane deposited from CCl$_4$



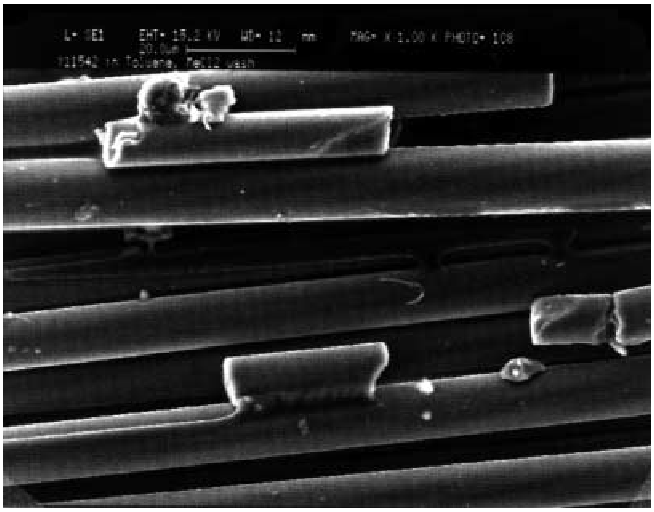


Fig. 10 Scanning electron micrograph of E-glass fibres treated with ureidosilane deposited from toluene

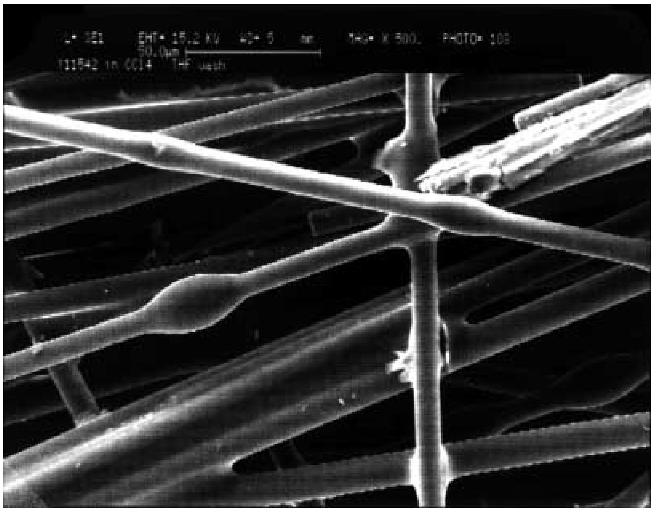


Fig. 11 Scanning electron micrograph of E-glass fibres treated with ureidosilane deposited from CCl_4

nitrogen/silica ratio (N/Si) as the samples progressed through the wash procedure (Fig. 5a, b). Ureidosilane deposited from toluene did not demonstrate solvent entrapment in the lower layers.

Ureidosilane deposited from CCl_4

Almost 4% by weight of ureidosilane was detected on the surface of E-glass fibres when CCl_4 was used as a deposition solvent as opposed to 2.5% from toluene (TGA). The increased mass loss was an anomalous result. ESCA and DRIFT both indicated that silane was removed as the samples passed through the washing sequence. Ureidosilane deposited onto E-glass fibres from CCl_4 appeared to produce a solvent-swollen but condensed network. The network was possibly a repository for solvent not removed by drying at 120 °C.

The ESCA results inferred that the high vacuum conditions used removed the remaining solvent. A possible exception being after the methanol wash when large amounts of C1*s* and concurrent N1*s* reduction (Table 5), but constant levels of $C=O$ (Fig. 5a), were detected.

The binding energy differences between O1*s* and Si2*p* (Table 6) suggested a patchy surface. Aluminium was detected in the samples deposited from CCl_4, yet aluminium was not detected in the E-glass fibres treated with ureidosilane in toluene (Table 3). These apparently contradictory facts can be explained by the presence of aluminium in the upper layers of siloxane deposited from CCl_4, which assisted in the formation of a condensed network.

Comparison of the OCH_3/CH_2–Si ratios indicated that hydrolysis of $Si(OCH_3)_3$ to $Si(OH)_3$ had occurred (Fig. 7). The reduction in the IEP as the sample passed

Table 5 Concentration of elements (ESCA) detected on the surface of E-glass fibres treated with γ-ureidopropyltrimethoxysilane deposited from CCl_4. *nd*: not detected

	CCl_4	Dichloromethane	Acetone	Tetrahydrofuran	Methanol
O1*s*	29.2	225.2	21.74	22.38	17.96
C1*s*	45.74	57.32	58.72	58.63	71.92
N1*s*	11.65	12.77	12.22	9.34	3.64
Si2*p*	6.71	7.39	7.31	9.66	6.48
Al2*p*	6.7	nd	nd	nd	nd

Table 6 Difference in binding energies (ESCA) between O1*s* and Si2*p*, deposition solvent CCl_4

	CCl_4	Dichloromethane	Acetone	Tetrahydrofuran	Methanol
O1*s*	531.8	532.1	531.8	532.1	532
Si2*p*	102.1	102.3	102	102.1	102.1
Difference	429.7	429.8	429.8	430	429.9
Surface	Patchy	Silane	Silane	Silane	Silane

through the wash sequence indicated that the surface consisted of a condensed Si–O–Si network [Si(OH)$_3$ to Si–O–Si].

Conclusions

Ureidosilane deposited from CCl$_4$ formed a solvent-swollen condensed network, whilst when toluene was used as a deposition solvent minimal (if any) condensation occurred. Both solvents gave a ureidosilane surface after initial deposition; the loosely bound ureidosilane was easily removed by subsequent solvent washes.

TGA and ESCA results implied that small amounts of methanol may have been retained in the lower layers of the silane network deposited from CCl$_4$ after the methanol wash.

Zeta potential results indicated that ureidosilane, when deposited from toluene and CCl$_4$, was present at the surface in two orientations: the first (deposited from toluene and CCl$_4$) mainly having the ureidogroup uppermost; the second (after passing through the solvent wash sequence) consisting of Si–O–Si (CCl$_4$) or SiOH (toluene) groups depending upon the deposition solvent.

Aluminium was detected at the surface of E-glass fibres treated with ureidosilane deposited from CCl$_4$ but not in those deposited from toluene. The aluminium was condensed into the siloxane network forming a condensed aluminosiloxane.

Because they have solubility parameters close to that of the silane, both toluene and CCl$_4$ were reasonably "good" solvents for the silane; this resulted in large quantities of silane being deposited.

DRIFT analysis confirmed the hydrolysation of the methoxy group to silanols, whilst the reduction in the IEP with washing solvent (CCl$_4$ samples) indicated that condensation of the silanols had occurred.

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