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Characterization of siloxane films on titanium substrate derived from three aminosilanes

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The aim of this investigation was to study the siloxane, –Si–O–Si–, film formation on Ti substrate by using mono-, bis- and tris-aminosilanes. The ultimate goal was to obtain a smooth, well-organized and stable siloxane film with suitable surface energy. Such films are expected to perform well in adhering resins to dental metal alloys when the films contain reactive functional groups. Aminosilanes were prepared as 0.5 vol.% solutions in dilute ethanol (50 vol.% ethanol in deionized water), with their natural pH of ∼9. The substrates were silanized in two ways: silane was allowed to react at room temperature or was cured for 1 h at 110 °C. The surface characterization was carried out by reflectance–absorbance Fourier transform infrared spectroscopy (RA-FTIR), x-ray photoelectron spectroscopy (XPS), contact angle measurement and atomic force microscopy (AFM). Siloxane film thickness measurements were not made. According to spectral analysis, all silanes indicated covalent bond formation with titanium. ≡Si–O–Ti≡ and ≡Si–O–Si≡ bonds were clearly seen in the spectra, suggesting that chemical retention had taken place. After curing at elevated temperature, the spectral bands seemed to be stronger than those on samples cured at room temperature. Curing of hydrolyzed silanes at elevated temperature seemed to enhance the siloxane layer formation, derived from aminosilanes, on the Ti substrate. This might have an influence on the hydrolytic stability of organosilane-promoted adhesion between Ti and dental resins.

KEYWORDS: silane; dental materials; titanium; adhesion; surface characteristics

INTRODUCTION

Titanium and titanium alloys are widely used materials in dentistry and medicine.[1] Titanium can be used in crowns, fixed partial dentures and implants. Titanium and its alloys are considered superior because of their chemical resistance to corrosion and erosion, their relatively low price and their biocompatibility, which is derived from a thin, dense oxide layer.[2] Titanium has several oxides (e.g. TiO, Ti_2O_3, Ti_3O_5 and TiO_2), of which TiO_2 in the form of rutile is thermodynamically stable whereas anatase and brookite are not.[3,4]

Different trialkoxysilane coupling agents are used for improving adhesion between metals (e.g. Ti, Co–Cr–Mo alloys) and composite resins, as well as in prosthetic appliances.[5,6] The most commonly used silane in dental applications is 3-methacryloxypropyltrimethoxysilane (MPS), which is a monofunctional silane with one silicon atom in its molecular structure. It has three methoxy groups ($-OCH_3$) and as an organofunctional substitute it has a methacrylate group bound via a propyl link ($-CH_2CH_2CH_2-$) to the silicon atom (Fig. 1, structure D). Commercial dental MPS is supplied pre-hydrolysed, usually as 1–2% MPS in 90–95% ethanol.[7] Aminosilanes are known coupling agents for thermosets, e.g. for acrylate, epoxy, phenol-formaldehyde, polyacrylate, polyimide, methylmethacrylate, urea-formaldehyde and urethane resin applications.[8] Recently, efforts to decrease polymerization shrinkage of restorative materials have been made by dental manufacturers. The epoxy-ring-opening-based so-called cationic restorative materials have been evaluated as known, potential, low-shrinkage materials.[9]

Before appliance as a coupling agent, inactive trialkoxysilanes (hereafter referred to as silanes) have to be diluted and hydrolysed (activated)

$$R'-Si(OR)_3 + 3\,H_2O \longrightarrow R'-Si(OH)_3 + 3\,R-OH \qquad (1)$$

The reaction is catalysed by acid (oxonium ions, H^+) or hydroxide ions (OH^-), or it can occur spontaneously in water (some aminosilanes). Labile, acidic silanol groups (–SiOH) are formed. Silanol groups condense and form dimers

$$R-Si(OH)_3 + R-Si(OH)_3 \longrightarrow R-Si(OH)_2-O-Si-(R)(OH)_2 + H_2O \qquad (2)$$

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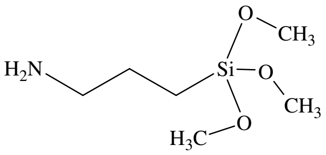
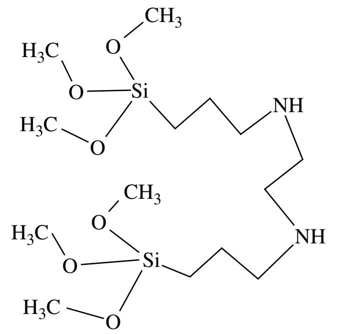


(A)



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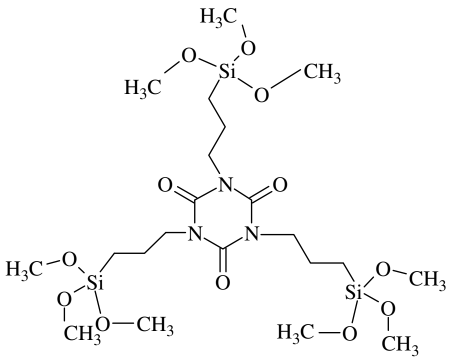

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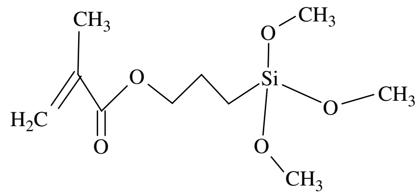

(D)

Figure 1. Molecular structures of the silanes used in this study. (A) 3-aminopropyltrimethoxysilane (APS) is a monofunctional aminosilane and a primary amine). (B) Bis-(3-trimethoxysilyl)propyletylenediamine (BPEA) is a bis-functional aminosilane and a secondary amine. (C) Tris-(3-trimethoxysilylpropyl)isocyanurate (TPCY) is a tris-functional aminosilane and a tertiary amine. (D) 3-Methacryloxypropyltrimethoxysilane (MPS) is a conventional silane for comparison.

A branched siloxane layer consisting of siloxane bonds (–Si–O–Si–) is formed from dimers that condense further, to form oligomers. Titanium has an extremely thin outer metal oxide layer with hydroxyl groups (–OH), thus enabling the formation of ≡Si–O–Ti≡ bonds.[10] Thermal curing is known to increase the cross-linking of silanes to form a siloxane film onto various metal surfaces, which has been reported recently for 3-glycidoxypropyltrimethoxysilane[11–14], aminosilanes[15] and a non-functional bis-1,2-(triethoxysilyl)ethane.[16] A non-functional silane molecule lacks the polymerizable organic part.

Silanol groups react to form one siloxane bond originating from one molecule with the inorganic substrate[17] or two or three siloxane bonds.[18] With the formation of chemical bonds between silane molecules and, in general, with a metal M substrate (e.g. titanium, cobalt, chromium) covered with hydroxyl groups, ≡Si–O–M bonds are formed. The hydrophobic siloxane layer is usually tens of molecular layers thick, depending on the silane concentration.[19] The organofunctional end of a silane molecule can polymerize covalently with monomers of the composite. All these bonds are of covalent nature, although silanes also can form hydrogen bonds.[17,20] Silane coupling agents form covalent bonds at the E-glass/resin interface, which has been observed by means of labelled (radioactive) pre-hydrolyzed silanes.[21]

Aminosilanes might be promising alternatives for the monofunctional MPS silane in dental applications because they can be obtained also in bis- and tris-functional forms. Monofunctional aminosilanes have been used as coupling agents for, e.g. epoxide and isocyanato-type resins, which have been suggested as future dental materials.[20] To the best of our knowledge, bis- and tris-functional aminosilanes have not been studied widely in conjunction with dental materials. The organofunctional trialkoxysilanes can be thought to be ammonia (NH_3) derivatives. The monofunctional 3-aminopropyltrimethoxysilane is a primary amine that has only one hydrogen atom substituted with the trimethoxysilylpropyl group. The bis-functional silane bis-(3-trimethoxysilylpropyl)ethylenediamine has two silicon atoms in the structural hydrocarbon chain and two amino groups; it is also a secondary amine. Tris-(3-methoxysilylpropyl)isocyanurate contains three silicon atoms attached to a heterocyclic carbon-nitrogen ring and can be classified as a tertiary amine, i.e. all hydrogen atoms of the amine group are substituted (Fig. 1, structures A–C).

Structurally, all the aminosilanes in this investigation have three methoxy groups ($-OCH_3$) attached to the silicon atom via a propyl group ($-CH_2CH_2CH_2-$) between the silicon and nitrogen atoms. Aminosilanes, in particular 3-(trimethoxysilyl)propylamine (also named 3-aminopropyltrimethoxysilane, APS), are widely used as adhesion promoters in applications between E-glass fibres and the epoxy composite resin in a reinforced composite matrix.[22,23] Aminosilanes are neutral or slightly basic silanes and are known to be stable in high-concentration solutions over long periods. The pH suitable for aminosilane deposition is 8–10 and acid is not needed as a catalyst in the solvent.[24] Calcium carbonate filler can be treated successfully with aminosilanes for polypropylene composites.[25] It is known that fusion between titanium and ceramics is not without problems.[26] During ceramic fusion, absorption of oxygen, hydrogen and nitrogen gases into the interstitial sites of the titanium lattice results in interstitial embrittlement, which can lead to low mechanical properties.[27] A way of overcoming this problem is to use a veneering composite resin instead of ceramics on titanium. Surface treatments such as tribochemical coating with a silane can enhance attachment of the composite resin to an adequate level.[28] Silanization of ground and polished Ti has been studied recently.[29]

The hypothesis was that bis- and tris-aminosilanes might form better-performing siloxane films on titanium substrate than mono-aminosilane, on the basis of their better cross-linking abilities due to the increasing amount of silicon atoms (i.e. functionality) in one molecule.

EXPERIMENTAL

Aminosilanes

For these studies, 0.5 vol.% solutions of 3-aminopropyltrimethoxysilane (APS from Merck, Darmstadt, Germany, *purum*, b.p. 80 °C 8 mmHg, flashpoint 83 °C), bis-(3-trimethoxysilyl)propyletylenediamine (BPEA from ABCR, Karlsruhe, Germany, 62% in methanol, flashpoint 11 °C), and tris-(3-trimethoxysilylpropyl)isocyanurate (TPCY from ABCR, Karlsruhe, Germany, *purum* 95%, flashpoint 102 °C)[30] were used without further purification. The silane amount was measured and rapidly moved to 25-ml polyethylene bottles, followed by the addition of 50 vol.% ethanol (Ethanol Anhydricum, Primalco, Helsinki, Finland, >99.5%) solution with deionized grade I water of electrical resistivity 18.6 MΩ · cm. The natural pH of APS, BPEA and TPCY was ~9. The sealed silane solutions were allowed to hydrolyse for 1 h at room temperature (20 °C).

Two or three drops of the silanes were brushed (a new brush used each time) onto titanium coupons and gently air-dried with oil-free compressed air following a clinical procedure (in dental laboratories and at chair-side), using the same amount of silane to form the siloxane films.[31] The samples were silanized at room temperature and cured either at room temperature (15 min) or at 110 °C (1 h). One hour of curing was selected, based on the silanization procedures described in the literature.[8]

Titanium

Planar, commercial pure (c.p.) grade 2 Ti coupons (Permascand, Ljungaverk, Sweden; 20 mm × 40 mm × 1 mm) were ground (1200 grit), washed and rinsed with deionized water in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing, Kearny, NJ, USA) and degreased with ethanol and acetone.

Fourier transform infrared spectroscopy

Spectral analysis was performed throughout the spectral range (4000–600 cm^{-1}) by reflectance–absorbance Fourier transform infrared spectroscopy (RA-FTIR; Perkin Elmer Spectrum One spectrometer, Perkin-Elmer, Beaconsfield, UK), using a variable-angle specular-reflectance monolayer/grazing angle accessory (Specac, Smyrna, GA, USA). A liquid-nitrogen (−196 °C, STP)-cooled $HgCdTe_2$ detector was used. The grazing angle was 80°, the number of scans was 32, the scan speed was 0.50 cm s^{-1} and the resolution was 2 cm^{-1}. This accessory chamber was open to ambient air conditions. The spectral subtraction capability of the spectrometer enables selective monitoring of the formation and deformation of different relevant bonds: the spectra are processed mathematically (including normalizing, baseline correction and data tune-up) to make the spectra comparable and to minimize noise. The spectra were examined visually, taking special interest in the spectral range of 4000–600 cm^{-1} reported to be characteristic for organosilanes and aminosilanes (Tables 1 and 2).

X-Ray photoelectron spectroscopy

The chemical composition of the outermost part of the silanized titanium samples was analyzed by XPS (Perkin-Elmer PHI 5400 ESCA System Spectrometer, Perkin-Elmer, Eden Prairie, USA). The XPS measurements were carried out at a base pressure of 1×10^{-8} Torr using an Mg Kα x-ray ($\lambda = 1253.6$ eV) source. The electron analyser pass energy in the XPS high-resolution scans was 35.75 eV and the analysis area was 4×4 mm^2. The photoelectron take-off angle was 45°. The UNIFITTU (University of Turku, Laboratory of Material Science) software (version 2.1) was used for peak fitting and quantitative chemical analysis, applying sensitivity factors given by the manufacturer of the instrument. The high-resolution spectra were charge-compensated by setting the binding energy (BE) of the C 1s contamination peak to 284.6 eV.

Surface free energy and wettability

The changes in wettability due to silanization were followed up by sessile drop dynamic contact angle (DCA) measurements using a FIBRO 1100 DAT dynamic adsorption tester (FIBRO System, Stockholm, Sweden). Contact angles were determined for water and ethyleneglycol, which have different surface tensions and polarity values. The measurements obtained were used to calculate the surface free energies of the surfaces by the two-liquid-phase method, utilizing the software provided by the manufacturer. Calculations are based on the modified Young's equation.[32]

Surface roughness

The surface topography and roughness were determined by non-contact tapping mode atomic force microscopy (AFM) using a NanoScope III multimode microscope (Digital Instruments, Santa Barbara, USA). The ultrasharp silicon cantilever used was 125 μm in length with a resonance frequency of ~325 kHz. The tip height was 15–20 μm with a nominal radius of curvature of <10 nm. All the measurements were carried out in ambient air conditions. Quantitative measurements of the local root-mean-square (rms) surface roughness, which defines the height fluctuations in a given area, were determined from the 50×50 μm^2 scans using the software provided by the manufacturer.

Table 1. Significant infrared absorption frequency regions for some trialkoxysilanes[20,41–43]

Frequency (cm^{-1})	Infrared spectroscopic group assignment
3740	Free Si–OH stretching
3740–3500	Bridged Si–OH stretching
3690	Free hydroxyl, –OH
3400–3200	Hydrogen-bonded –OH
3280	Free water, H_2O
3385–3340	Bonded silanol, ≡Si–OH
2940, 2840	Stretching (asymmtric and symmetric) ≡Si–O–CH_3
2840	≡Si–O–CH_3
1735	Carbonyl =C=O stretching
1638	$SiO_2 \cdot nH_2O$ (H–O–H bending motion)
1480–1300	CH_2, CH_3 bending
1260	≡Si–CH_3
1250–1220	≡Si–$CH_2CH_2CH_2CH_2$.... (long chain)
1250–1020	Si–O–Si asymmetric stretching vibration
1190, 1100–1080, 1087, 818	≡Si–O–CH_3
1130–1000	≡Si–O–Si≡ siloxane bonds, often broad and complex
1080–1040	–Si–O–Si–O–Si– (long chains)
1050	Inorganic silicates
1000–900	Si–O–Metal bonds
925–950	–Si–O–Ti– siloxane bonds to titanium
880	Si–OH, Si–O stretching
487	Inorganic silicates (also ≡Si–O–CH_2CH_3 symmetric deformation)

RESULTS

Fourier transform infrared spectroscopy

The infrared spectra for deposited silanes taken after the condensation reactions on metal surfaces (registered with RA-FTIR) showed strong, broad, but usually complex ≡Si–O–Si≡ (siloxane) bands in the region 1130–1000 cm^{-1}. Also, corresponding ≡Ti–O–Si≡ bands could be seen at 900–1000 cm^{-1}. The spectra showed strong siloxane signals when cured at a high temperature of 110 °C (Fig. 2). As an example, BPEA silanization at different temperatures is shown (Fig. 3). Infrared spectral bands for the organic part of the condensed silane molecules were detected (although as weak vibration bands) at ~2905 cm^{-1} for –CH and weak bands at 1480–1300 cm^{-1} were assigned to the bending mode of –CH_2, and –CH_3 groups in the molecule.

X-ray photoelectron spectroscopy

Due to the silanization, the titanium peak disappeared from the XPS spectra, indicating full silane coverage of the surface. Thus, the siloxane layer was too thick for the bonding between the silane and titanium substrate to have been observed. The spectra consisted of C, O, N and

Table 2. Significant infrared absorption frequency regions for amino groups in silanes (R = radical)[20,24,37,38]

Frequency (cm^{-1})	Infrared spectroscopic group assignment
3400–3200	N–H stretching
3370, 3290	NH in the CO_2 adduct
3214	Stretching NH_2
2500	Ammonium hydrogen carbonate NH_4HCO_3 (–OH)
2150	NH_2^+ in the ring structure
1640–1630	Carbonyl =CO of carbamates R–$NHCO_2$–RNH_3^+
1630	Hydrogen carbonate HCO_3^-, a shoulder
1609	NH_2 deformation
1600	Deformation band, free amine groups
1590, 1595	Bending of free amino groups
1500–1700	Carbonyl region for amino adducts
1575	Hydrogen-bonded amines (siloxane bonds formed)
1575	Carbamate antisymmetric and symmetric deformation of NH_3^+
1560–1640	Free R–NH_2
1500–1050	NH_3^+, evidence of interaction with the surface
1480	Antisymmetric and symmetric deformation of –NH_3^+ and HCO_3^-
1250–1000	Ester portion of carbamates –CO–O–C

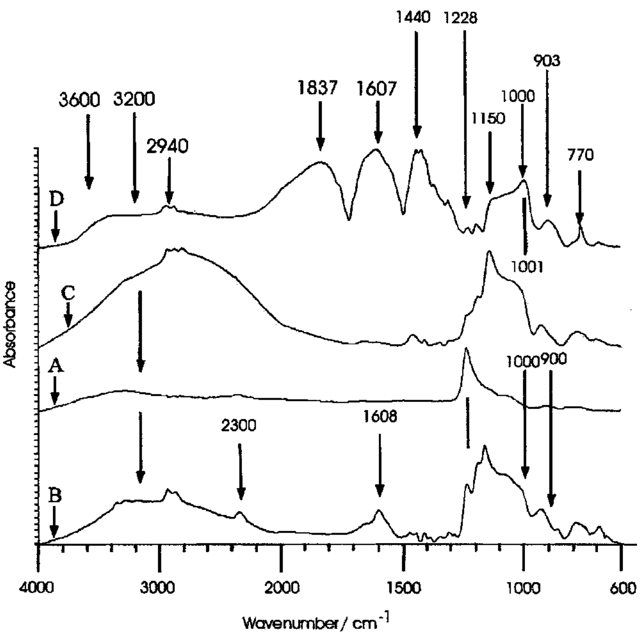

Figure 2. The FTIR spectra of non-silanized Ti (A), APS-silanized Ti (B), BPEA-silanized Ti (C) and TPCY-silanized Ti (D). All silanized samples were cured at 110 °C. Abbreviations: APS = 3-aminopropyltrimethoxysilane; BPEA = bis(3-trimethoxysilyl)propylethylenediamine, TPCY = tris(3-trimethoxysilylpropyl)isocyanurate.

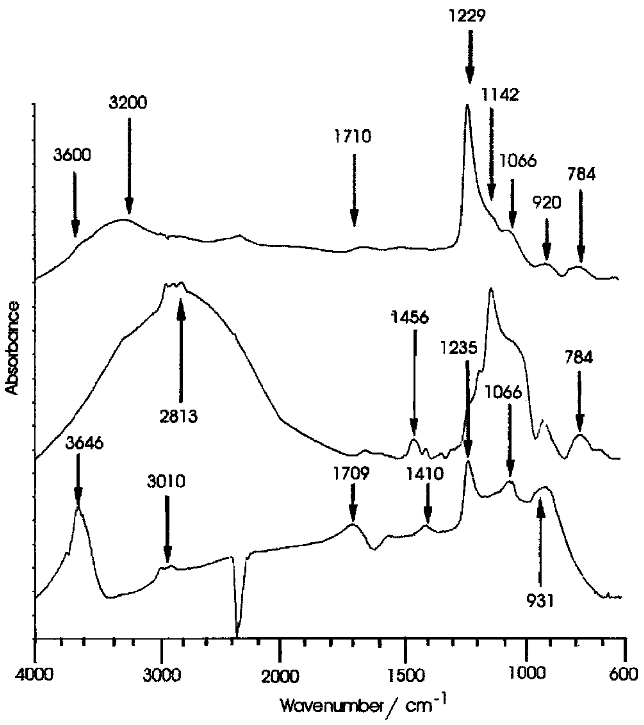

Figure 3. The FTIR spectra of non-silanized Ti (A), Ti silanized with BPEA and cured at room temperature (B) and Ti silanized with BPEA and cured at 110 °C (C). For meanings of abbreviations, see Fig. 2.

Si components. The binding energy of Si was ~102.2 eV for all the samples, which corresponds to the siloxane (CH_3–Si–O–Si–CH_3). The high-resolution nitrogen spectra consisted of two different peaks (Fig. 4 and Table 3). The peak at 399.1 eV was related to free amino groups (–NH_2) and the peak at 400.5 eV to protonated amino groups (NH_3^+).

Surface free energies and wettability

The silane treatments resulted in more hydrophobic surfaces than the control titanium, as observed from the increase in water contact angles (Table 4). The APS-silanized and room-temperature-cured Ti surface was unstable and the water drop removed the siloxane film from the surface, resulting in a decreased water contact angle and increased surface free energy. Consequently, its values were not included in the results. Otherwise, no significant differences were observed in the water contact angle between the silanized samples. The silane treatment significantly decreased (~25%) the surface free energy of the surface compared with the control titanium surface, although no significant differences were observed between the different silane treatments. In addition, the surface free energy did not vary due to the drying at 110 °C for any of the aminosilanes used.

Table 3. Binding energies (eV) of Si and N species obtained from the high-resolution XPS data for silanized Ti samples (percentage of individual nitrogen components in parentheses)

Silane[a]	Curing[b]	Si 2p	N 1s
APS	RT	102.4	399.0 (83.5) 400.4 (16.5)
APS	OC	102.3	399.1 (82.7) 400.5 (17.3)
BPEA	RT	102.3	399.2 (75.4) 400.4 (24.6)
BPEA	OC	102.1	399.2 (82.6) 400.7 (17.4)
TPCY	RT	102.2	399.5 (18.3) 400.8 (81.7)
TPCY	OC	102.1	399.4 (4.9) 400.8 (95.1)

[a] APS = 3-aminopropyltrimethoxysilane; BPEA = bis(3-trimethoxysilyl)propylethylenediamine; TPCY = tris(3-trimethoxysilylpropyl)isocyanurate.
[b] RT = cured at room temperature; OC = cured in the oven, at 110 °C.

Table 4. Water contact angles and surface free energies for different silane treatments

Sample and treatment[a]	Contact angle of water (°)	Surface free energy (mN m^{-1})
Ti (control)	48.6	51.72
Ti + APS + OC	61.8	42.90
Ti + BPEA + RT	61.6	43.09
Ti + BPEA + OC	62.8	41.91
Ti + TPCY + RT	68.1	40.15
Ti + TPCY + OC	63.8	43.81

[a] Abbreviations are listed in footnotes to Table 3.

Surface roughness

The AFM images of the differently silanized titanium surfaces showed clear changes in surface roughness, depending on the silanization (Fig. 5). The surface roughness decreased in the samples that were treated at elevated temperature compared with those treated at room temperature. In addition, the surface roughness of the samples treated at elevated temperature decreased in the series BPEA (214 nm), APS (88 nm) and TPCY (15 nm). The TPCY-silanized Ti sample, treated at 110 °C was clearly the smoothest. The TPCY-silanized surface cured at room temperature could not be measured with AFM owing to the 'stickiness' of the surface, which caused dampening of the tip oscillation and thus impeded the imaging.

DISCUSSION

In general, aminosilanes are readily soluble and have an unlimited stability. When dilute organofunctional aminosilanes are prepared at up to 50 vol.% water in ethanol at their natural pH (~9), the products immediately form oligomers that retain solubility in moderate concentrations. Neutralized aminosilanes dissolve quickly in water but form micelles of non-hydrolysed silanes. Silanes can be provided in 50 vol.% ethanol solutions.[33] 3-Aminopropyltrimethoxysilane hydrolyses and condenses self-catalysed in solution: it forms aggregates of oligomers of sub-micrometre diameter that can be broken up using alcohol in solution.[34] Aminosilanes are usually applied at pH 8–10[17,20,35,36] but pH ~4 has been used for E-glass fibres. Protonated aminosilanes have better solubility in water–alcohol mixtures.[15,22] Aminosilanes can form ring structures of ion-like oligomers in solution, so-called zwitterions. This might explain the unique solubility of trialkoxyaminosilanes.[20] However, aqueous APS solution

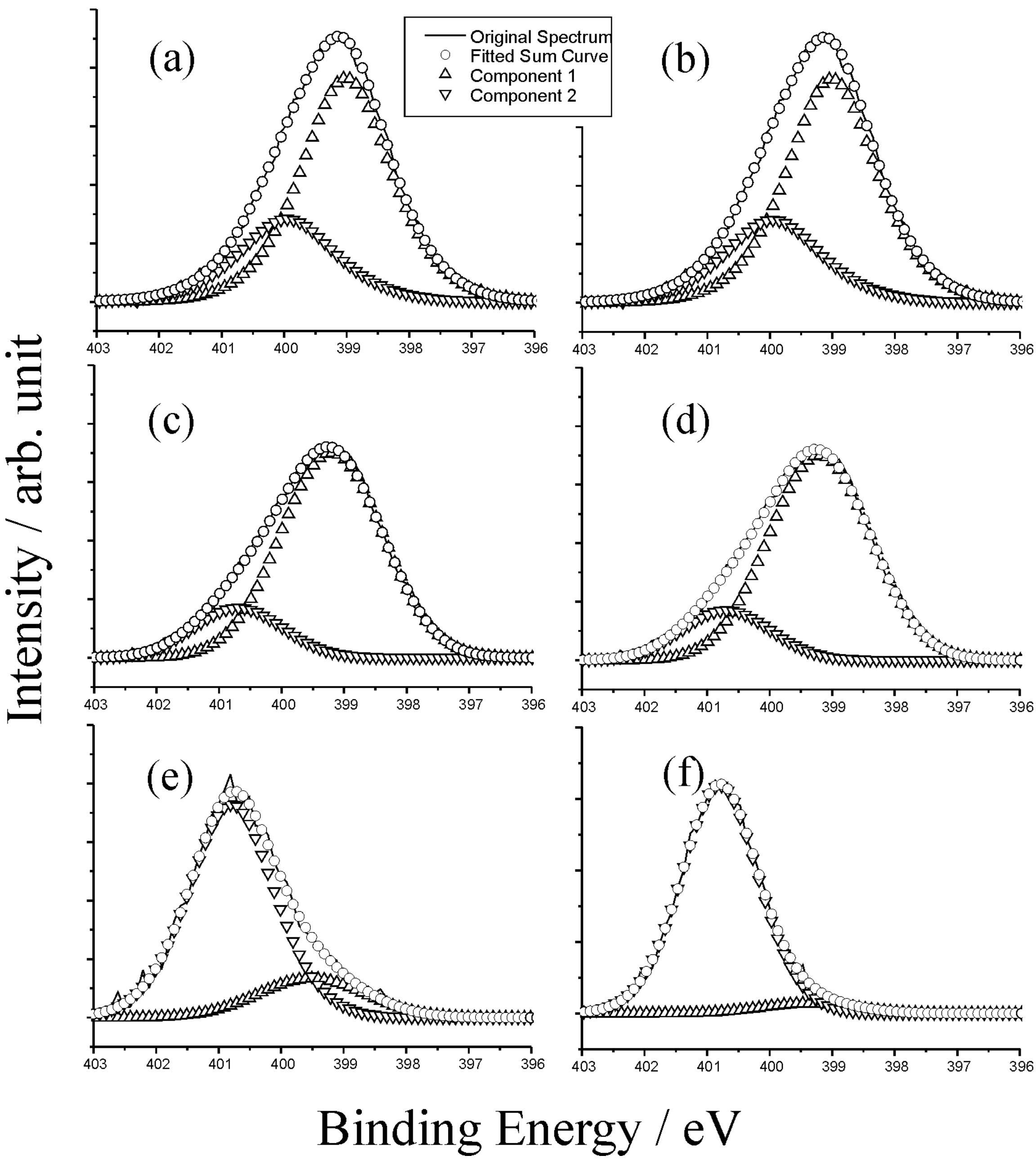

Figure 4. Fitted high-resolution N 1s spectra of titanium silanized with APS at room temperature (a), APS at 110 °C (b), BPEA at room temperature (c), BPEA at 110 °C (d), TPCY at room temperature (e) and TPCY at 110 °C (f). For meaning of abbreviations, see Fig. 2.

can react with atmospheric carbon dioxide to form carbamate salts ($R{-}NHCO_2{-}RNH_3^+$)[37] or hydrogen carbonates (HCO_3^-).[38]

Condensation reactions and reactions with the Ti surface

A non-treated titanium sample and samples cured at room temperature and at 110 °C are shown in Fig. 2 for each of the aminosilanes in question. Figure 2 shows a broad band for hydroxyl groups on the surface at ~3600 cm^{-1} and a ≡Si–O– hydrocarbon (methoxy) chain band at 2900 cm^{-1}, but the carbonyl peak at ~1710 cm^{-1} (from acetic acid atmospheric-adsorbed carbon dioxide) could not be seen clearly. Each strong band at 1237–1224 cm^{-1} was due to Ti–O vibrations. However, these overlapped with peaks at 1236–1066 cm^{-1}, showing the siloxane layer and its bonds. The ≡Si–O–Ti peak was seen at ~919 cm^{-1}.

The BPEA-treated titanium samples showed remaining hydroxyl groups (probably water molecules trapped inside the siloxane film) at 3694 cm^{-1}, a ≡Si–O–hydrocarbon chain band at 2923 cm^{-1} and small bands at 1664 cm^{-1} and 1286 cm^{-1} (ester) that may have been due to other NH-type vibrations. Siloxane and metal–oxygen peaks were seen at 1224–1038 cm^{-1} and 1224 cm^{-1} and a Ti–O band also could be seen. The ≡Si–O–Ti bonds were related to the peak at ~916 cm^{-1}.

The ring structure bands at 2126 cm^{-1} (nitrogen in the ring), 1691–1607 cm^{-1} (NH deformation) and 1837 cm^{-1} (ring structure with both N and C) for the TPCY's heterocyclic ring structure (on the silanized samples) showed the

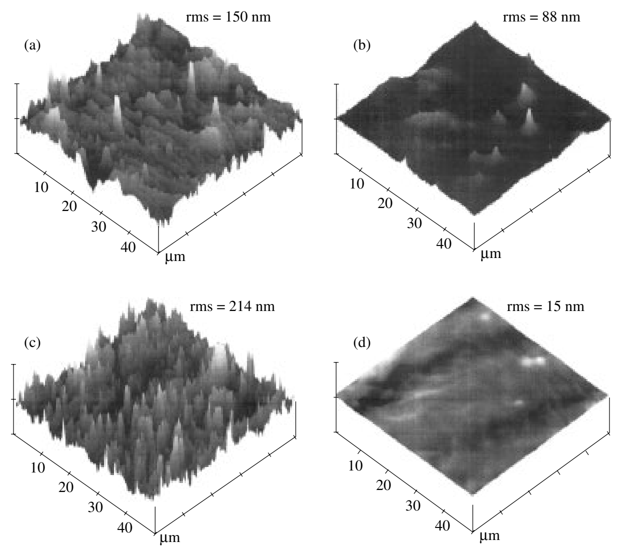

Figure 5. The AFM images of control titanium (a) and APS (b), BPEA (c) and TPCY (d) silane-treated titanium surfaces cured at 110 °C, with their corresponding surface roughness (rms) values. Image size is $50 \times 50\ \mu m^2$ and the z range is 1 μm. For meanings of abbreviations, see Fig. 2.

greatest differences when this spectrum was compared with the previous two spectra. Otherwise, the following spectral peaks could be seen: a facial hydroxyl group peak at 3646 cm^{-1}, ≡Si–O–CH_3 at 2942–2900 cm^{-1}, a siloxane stretching region at 1050–1000 cm^{-1}, a peak at 1237 cm^{-1} for ≡Ti–O–, ≡Si–O–Ti≡ stretching at ~925 cm^{-1} and a peak at 766 cm^{-1} that might be for ≡Si–C vibrations. The peak at 925 cm^{-1} also might be due to non-cured, residual ≡Si–OH groups, especially if the silane has possessed ethoxy groups (930–840 cm^{-1}).[16,20] However, the curing temperature and time applied in this study rather suggest that it is due to ≡Si–O–Ti≡ stretching.

According to Plueddemann,[20] siloxane bonds appear immediately along with a shift in the NH_2 deformation mode band from 1600 to 1575 cm^{-1}. However, this phenomenon could not be seen in the hydrolysis spectra, apparently due to the short monitoring period.

The spectral peaks suggested that all aminosilanes effectively formed a siloxane network when cured at 110 °C compared with curing at room temperature. Elevated temperature speeded-up the excess alcohol water evaporation and created faster siloxane bonds. There was no spectral evidence that hydrolyzed aminosilanes could have decomposed at the high temperature. Aminosilanes can, in principle, form bonding to the inorganic matrix (e.g. silica) through the nitrogen atom that has a free electron pair by forming an amino bond,[39] or through a bond of ionic character to the inorganic substrate in an acidic medium when the aminosilane is protonated. This effect has not been included in this study but could be a future research activity. Some of the FTIR spectra might have needed to be recorded with higher sensitivity.

Surface characteristics

The outermost surface characteristics were determined by XPS, contact angle and AFM measurements. Siloxane film thickness measurements were not made. The XPS analysis showed that the observed silica appeared in the form of siloxane, which is in accordance with the RA-FTIR results. Thus the studied silanes were 100% hydrolyzed even on the outermost surface (Fig. 6 and Table 3). In addition, free NH_2 groups were observed to be the dominant form of nitrogen on the surface, except in the TCPY silane, where, in accordance with its molecular structure (Fig. 4), the observed nitrogen appeared mostly in protonated form (NH_3^+). The protonated form was also evident on the APS and BPEA silanes. The protonated amino groups are protonated either by the acidic surface hydroxyl groups of the titanium substrates or by the intermolecular hydrogen bonding of amino and silanol groups. The amino groups also could be oriented towards the substrate, which could explain the observed nitrogen peaks. However, this explanation can be excluded because the titanium peak was not observed owing to the thick silane film that was formed.

The silanization treatments resulted in an increased hydrophobicity (i.e. increased water contact angle) of the surfaces when compared with non-silanized titanium metal. In addition, the surface free energy, which is a direct measure of surface properties and interfacial interactions such as adhesion, decreased due to the silanization. Although, in general, it can be said that low surface energy leads to low adhesion and high surface energy leads to high adhesion, these results are still promising and should be considered in conjunction with the energies of adhesive resins. Thus, the surface free energy measurements are helpful in making the optimum choice in future adhesion experiments with composite resins. In general, the contact angle and surface free energy results are also influenced by the surface roughness, which varied considerable between the silane treatments. It is thought that a smooth, rather uniform silane-coupling-agent-derived siloxane surface with functional groups (e.g. amino, epoxy, methacrylate, vinyl) would perform well as an adhesive surface in dental applications. A siloxane surface is always highly hydrophobic and it is a starting condition to silane-promoted adhesion.[15,17] The AFM images showed that the smoothest surface features were obtained with the oven-cured TPCY-silanized sample. The minimum shear bond strength for dental materials is 5 MPa, according to the ISO standard, and this should then be exceeded.[40]

CONCLUSIONS

The surface characterization of aminosilanes on a Ti substrate surface suggested that:

(1) Curing the silane at an elevated temperature resulted in more effective siloxane network formation than at room temperature, although the outermost surface consisted mainly of non-reacted ≡Si–O–CH_3≡ groups. The smoothest surface was obtained with tris-(3-trimethoxysilylpropyl)isocyanurate. The roughest siloxane films were obtained with bis-(3-trimethoxysilyl)-propyletylenediamine, at room temperature and at elevated temperature.

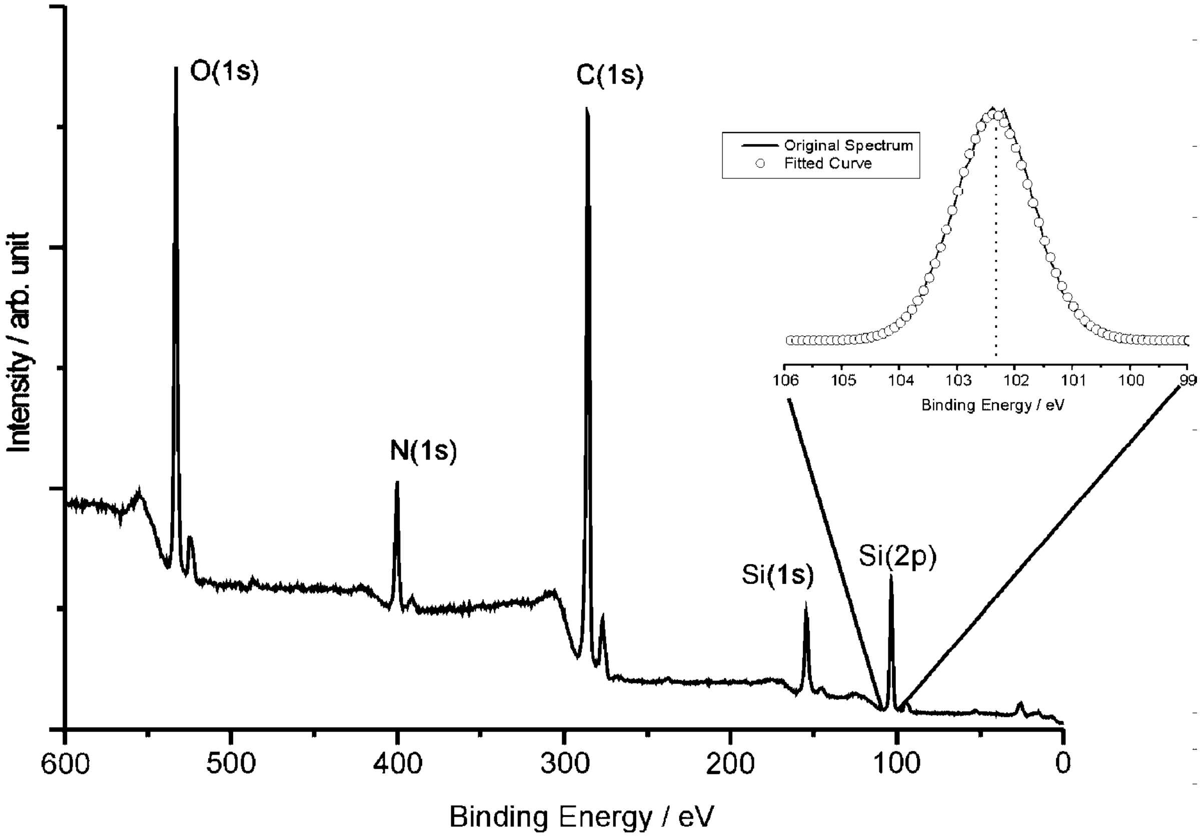

Figure 6. The XPS survey spectrum of titanium silanized with APS cured at room temperature. The inset shows the high-resolution Si 2p spectrum. APS = 3-aminopropyltrimethoxysilane.

(2) Oven-cured tris-(3-trimethoxysilylpropyl)isocyanurate gave the strongest ≡Si–O–Si≡ signals on the FTIR spectra. Also, oven curing always seemed to yield stronger FTIR signals than silanization at room temperature.
(3) The lowest surface energy values were obtained for tris-(3-trimethoxysilylpropyl)isocyanurate at both temperatures.

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