

Monitoring Chemical Changes on the Surface of Borosilicate Glass Covers during the Silanisation Process

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Abstract: *This work provides detailed spectroscopic, elemental and contact angle analyses for the treatment of borosilicate glass covers. The glass surface was first treated with strong acid to promote hydroxylation, followed by silanisation using 3-(trimethoxysilyl)propyl methacrylate. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to identify the chemical changes on the surface and energy dispersive x-ray analysis (EDX) analysis was used to further confirm any compositional changes of the surface elements. Hydrophobicity/hydrophilicity changes throughout the course of the modification were monitored using contact angle measurements, from which the surface free energy proved the consistency of the chemical modification performed.*

Keywords: Chemical changes, contact angle, hydroxylation, silanisation process

1. INTRODUCTION

It has been well established that glass surfaces consist of silanol groups.¹⁻³ These OH groups can be dehydrated at temperatures above 200°C but can attain partial reversible rehydration at decreasing temperatures.⁴ The generating of silanol groups on glass surfaces can be induced by various chemical treatments, including sulphochromic solution⁵, nitric acid⁶, NaOH⁷ and hydrogen peroxide:sulphuric acid⁸. With the generation of free silanol, a coupling agent can be introduced to incorporate sensing materials and various reagents. It is imperative that the supporting matrix and the reagent be covalently bound to the glass surface to ensure sensing durability and prevent leaching of the incorporated reagent.^{6,9} Most of the past work related to optical fibre sensors and biomolecular patterning has adopted this general method of fabrication. Surprisingly, there is a stark ambiguity in the nature of attachment of the supporting matrix to the glass surface because direct evidence is extremely rare. Yao et al.¹⁰ fabricated a protein microarray on a modified glass surface but revealed neither detailed features of the modification on the glass surface nor surface interactions with the protein molecule. By a similar nature, protein immobilisation was performed by Qin et al.¹¹ who proved glass surface

modification via x-ray photoelectron spectroscopy (XPS) analysis. Secondary evidence in the form of contact angle wettability was used to confirm the successful modification.^{7,12,13} However, it was noted that contact angle measurements are arbitrarily dependent on the user.¹⁴ Furthermore, because of the surface roughness and chemical heterogeneity, each sample gives a range of values within a tested surface.¹⁵ Prior to silanisation, the glass surface is normally pre-treated using "piranha solution" (a mixture of H₂SO₄ and H₂O₂). This solution is very corrosive and requires maximum care during use as well as disposal.

This work demonstrates direct evidence in the monitoring progress of borosilicate glass surface modification through hydroxylation followed by silanisation using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). The versatility of this method was further proven by the consistent data obtained in detecting the degree of modification when performed over an extended period. The initial hydroxylation stage was successfully performed using a simpler and safer route of avoiding the generally used "piranha solution". Energy dispersive x-ray analysis (EDX) and contact angle measurements corroborated well with the findings from the ATR-FTIR results.

2. EXPERIMENTAL

Materials: 3-(trimethoxysilyl)propyl methacrylate (TMSM), sulphuric acid Fixanal (0.1 mol), and acetone (reagent grade) were all purchased from Sigma Aldrich (Sigma-Aldrich Company Ltd, Dorset, UK). Borosilicate glass covers were purchased from VWR International with a size of 22 × 22 mm and a thickness number of 1.5.

Acid treatment: Glass covers of size 22 × 22 mm were gently polished using grade 1200 sand paper. They were then rinsed using acetone before use. The samples were soaked in a solution of sulphuric acid (30%) for six hours and 12 hours at room temperature. The glass samples were cleaned with deionised water until neutral and then rinsed with acetone, dried and stored in a vacuum desiccator.

Silanisation: A mixture of dried acetone (5 ml), TMSM (0.5 ml) and deionised water (0.5 ml) were mixed thoroughly in a round-bottom flask. This flask was enveloped in a black adhesive layer to avoid ambient light. The acid-treated glass was placed into the flask and left to stir at room temperature for 24 hours. The glass samples were then thoroughly rinsed with acetone, sonicated in acetone for 10 minutes, and left to dry in a vacuum desiccator prior to analysis.

2.1 Measurement

The sessile water drop procedure was performed to measure the surface contact angle using a 30 μL drop of deionised water. A pictograph was taken using a Pixelink PL-A6xx camera using three readings from each specimen. The image was processed using Linksys32 Ver 1.8.9 software. The surface free energy was calculated from the contact angle made by the glass surface with water and ethylene glycol as probe liquids using the Owens-Wendt-Kaelble equation¹⁶:

$$\gamma_1(1 + \cos \theta) = 2[\gamma_i^d \gamma_s^d]^{1/2} + 2[\gamma_i^p \gamma_s^p]^{1/2} \quad (1)$$

where γ_s is the surface free energy, γ_i^p and γ_i^d are the probe polar and dispersion components, respectively, and γ_s^p and γ_s^d are the glass polar and dispersion components, respectively. ATR-FTIR spectra were obtained using a Thermoscientific Nicolet 8700 in the range of 4000–600 cm^{-1} at 64 scans with 4 cm^{-1} resolution. For good contact, a rubber layer was placed between the pressure knob at 80 N and the glass sample to ensure maximum support onto the crystal prism. EDX measurements were performed on a JEOL JSM-6060 LV SEM at 600x magnification, an accelerating voltage of 20 kV and a working distance of 10 mm. The sample was coated with a 15 nm layer of gold. Three measurements were obtained at different spots and the averages were taken to compare with those of the untreated sample.

3. RESULTS AND DISCUSSION

General silanisation protocols on glass surfaces utilise piranha solution (70% sulphuric acid:30% hydrogen peroxide)¹³ as a hydroxylation agent. In this work, a simpler and safer method using 30% concentrated sulphuric acid as the hydroxylation agent, followed by a silanisation step, is presented. Despite its lower oxidation capability, at higher acid concentration under a longer duration, hydroxylation of a glass surface is equally achievable using this approach. The reaction scheme is shown in Figure 1.

The first step involves hydroxylation using an acid catalyst, which breaks the Si-O-Si linkages to yield free silanol groups. This was performed for six hours and 12 hours. Silanisation was then performed on the treated glass surface using TMSM as a silane coupling agent under aqueous acid medium over 24 hours at room temperature. Silanisation has been determined to first proceed by hydrolysis of the methoxy groups of TMSM, followed by condensation with the

hydroxyl group of silanol to form Si-O-Si bridges¹⁷. Compared to the less stable Si-O-C bridges, the thermodynamically stable Si-O-Si bridges could feasibly form at room temperature¹⁸. The three methoxy groups of TMSM could readily hydrolyse to form hydroxyl groups, which are susceptible to condensation with each other as well as the surface hydroxyl groups. The former would form a separate polymeric phase,¹⁹ which would be leached away during the sonication step. Thus, formation of a 2D network is possible between the neighbouring head of the hydroxyl group and the surface silanol.

3.1 FTIR Analysis

Because of the high glass transparency in the mid-IR region, the ATR mode of detection was used to obtain an improved spectrum. It was used to monitor and reveal the proposed reaction scheme above, see Figure 1.

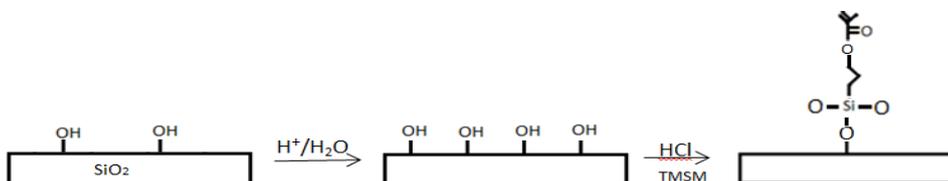


Figure 1: Proposed reaction scheme involved during acid treatment and silanisation.

No significant peaks were observed above 2500 cm⁻¹, which is likely a result of poor sensitivity of the evanescent radiation at shorter wavelengths used in this mode. Because the pressure applied was locked at 80 N and the thicknesses for all samples were nearly identical, the peak intensity likely signifies the intrinsic content of the detected functional groups. Another feature worth noting is that most of the peaks are broad, which was similarly observed when using piranha solution under ATR-FTIR mode⁸. In fact, these peaks arise from overlapping peaks of several chemical groups making up the glass material. The absorption intensity of the samples is highest after silanisation, followed by after acid treatment and lastly for the untreated sample. This trend of peak intensities demonstrates the corresponding chemical changes during the surface modification, which include the formation of C-H, C-O-C, Si-O⁻, and Si-O-Si groups as well as the breakage of Si-OH and Si-OMe bonds derived from hydroxylation and grafted TMSM. The peak in the range of 1080–1060 cm⁻¹ represents the Si-O-Si as well as C-O-C groups, which occur in the same region. Herein, the untreated and acid-treated (six hours) samples show lower peak intensities compared to the acid-treated (12 hours) and silanised samples. This observation is a result of the Si-O-Si group exclusively formed during the treatment. In the latter case, because of the additional contribution of C-O-C groups derived from TMSM, the peaks appeared higher in intensity.

Additionally, these peaks showed a small intensity difference between the six hours and 12 hours silanised samples. It is thus proposed that the silanisation has reached a saturation level after six hours, which results in only a small increase in peak intensity beyond this point. The 12 hours acid-treated sample showed much higher peak intensity in this region compared to the six hours acid-treated sample. It is believed that this result is attributed to the close proximity of the vicinal hydroxyl group, which affects recondensation. It has been observed previously that a fully dehydrated silanol groups will easily recondensed to form Si-O-Si linkages after adverse thermal treatment.⁴ Under the prolonged heat treatment and high acid concentrations used in this work, a similar reaction should be plausible and is consistent with the EDX results discussed below. A closer inspection revealed a shoulder peak at 970 cm^{-1} for all samples. This peak is the Si-O stretch of the isolated/geminal groups and the bands at 840 and 760 cm^{-1} have been assigned to the Si-O-H angle deformation modes^{20,21}. The presence of these peaks shows that not all silanol groups have been grafted by TMSM. No prominent peak at 1260 cm^{-1} was observed, which otherwise correspond to the $-\text{CH}_3$ bending in the case of silanised samples.²⁰ This result indicates that the methoxy groups of TMSM were mostly transformed into siloxane bridges during silanisation. This hypothesis was further substantiated by a reduction in peak intensity, forming a deep trough in the $827\text{--}800\text{ cm}^{-1}$ region, corresponding to $-\text{CH}_3$ rocking.²⁰

3.2 EDX Analysis

Further evidence of the successful modification is provided by the EDX analysis. The elemental analysis determined using EDX was used to monitor the successful chemical modification of the glass surface. EDX measurements at three spots in each sample were obtained under $600\times$ magnification with a sample density of 19.32 and a thickness of 15 nm . Figure 2 shows the SEM spectra for the surface morphology of the representative samples.

The surface morphology of the treated glass surface, either after six hours or 12 hours, did not differ significantly from the original sample at the same magnification in that they appeared smooth and homogeneous. In addition to carbon, oxygen and silicon, the EDX analysis revealed the presence of inorganic ions not exceeding 10% weight content.

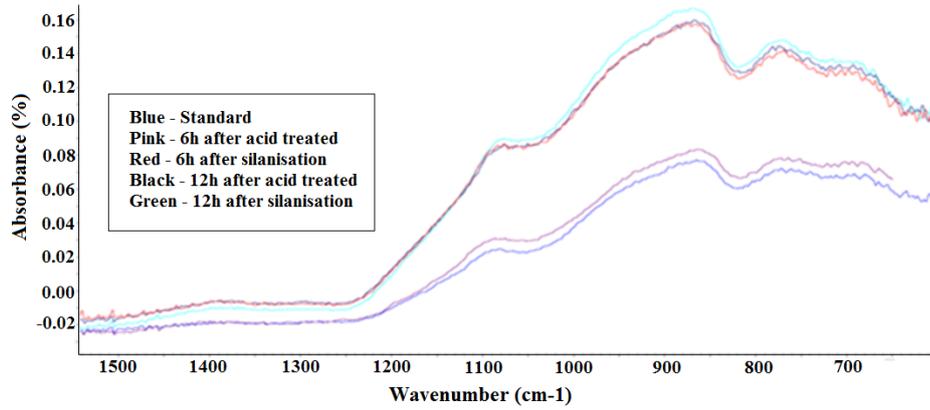


Figure 2: ATR-FTIR spectra of the pure sample and the sample after acid treatment and silanisation after six hours and 12 hours.

The changes in the weight percent content of carbon, oxygen and silicon are displayed in Figure 3.

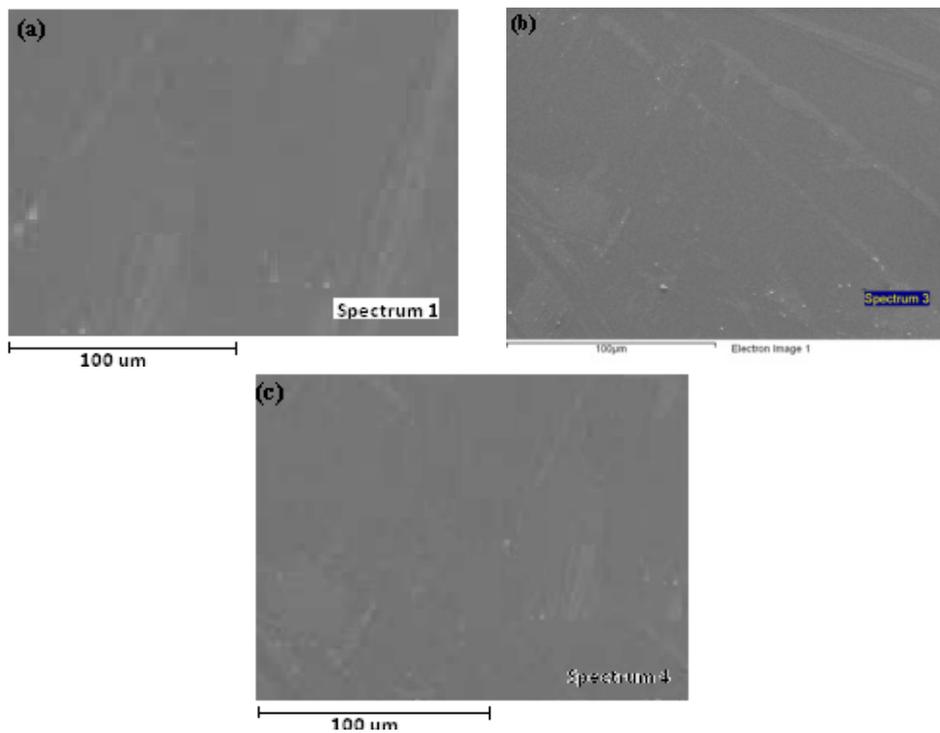


Figure 3: Representative SEM scans of the (a) original sample, (b) acid-treated sample after six hours and (c) acid-treated sample after 12 hours.

The silicon weight content is shown to decrease consistently throughout the treatment compared to that of the standard sample. This reduction establishes the occurrence of chemical modification through the introduction of TMSM molecules. As a result of the grafted acrylate molecules, the weight percent content of silicon is mostly lowered after silanisation, which is consistent with the increase in carbon content following silanisation. This process also induced a proportional increase in oxygen content because the TMSM contains five oxygen atoms per molecule. However, there is a reduction in the oxygen content after 12 hours compared to the six hours acid-treated sample. This result could possibly be attributed to the vicinal silanol groups, whose proximity affects partial recondensation by the release of water molecules during prolonged acid treatment.⁴ The process of silanisation also affects the further loss of surface oxygen atoms in the form of water molecules through condensation.

3.3 Static Contact Angle

The contact angle determines the degree of wettability of solid surfaces. In the case of using water as a probe liquid, this angle is dependent on the surface hydrophobicity/hydrophilicity. Several polar groups exist on the glass surface, including SiOH, SiO and SiOMe. A small contact angle implies a hydrophilic surface, whereas a larger angle corresponds to a hydrophobic surface. The changes in contact angle using deionised water as the probe liquid are shown in Figure 4.

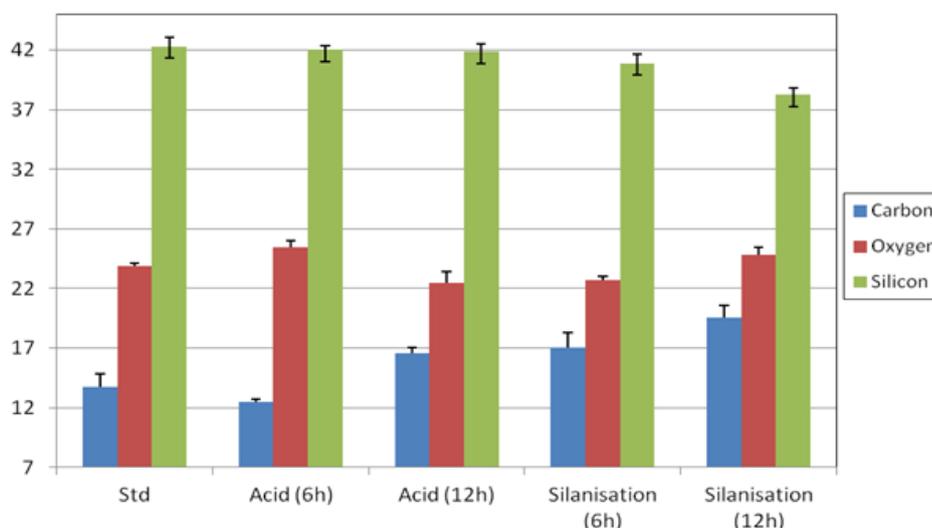


Figure 4: Weight percent changes of carbon, oxygen and silicon after acid treatment and silanisation processes.

The contact angle after acid modification shows the lowest values after a 12 hours duration compared to the other samples. This result implies that the glass surface is highly hydrophilic as a result of the formation of polar silanol groups. After silanisation, the contact angle values increased comparably to those of the original untreated sample. With the introduction of TMSM, the surface became increasingly hydrophobic because of the increase in its hydrocarbon content. Similar behaviour was observed in a series of acrylic copolymers for use in contact lens manufacturing.²² However, prolonged exposure of the surface to an ambient environment renders the glass surface increasingly hydrophilic. Thus, care is needed to perform the measurement under a dry enclosure. In this work, minimal exposure to ambient environment was ensured and the measurements were obtained promptly once the probe liquid was applied to the glass surface.

3.4 Surface Free Energy (SFE)

A range of glass surface free energies was recorded between 43.1 and 112.9 mJ/m².^{23,24} The wide range of values displayed by this material is attributed to the different chemical constituents present during their manufacturing, particularly at the surfaces. Differences in the use of probe solvent pairs as well as the method of calculation should also be taken into consideration.²⁵ In this work, the SFE was found to be 75 mJ/m² as described elsewhere.^{23,24}

The values of the surface free energies of water and glycerine were obtained from the literature, as given in Table 1, which were used to calculate the free surface energy of the treated glass surface. The changes in free surface energy of the glass surface treatment are plotted in Figure 5.

The SFE was observed to increase after acid treatment. This increase was much greater for the 12 hours treatment compared to that of the six hours treatment. This observation indicates that an increase in hydrophilicity results from the hydroxylation using an acid catalyst, which breaks the Si-O-Si linkages to yield free silanol groups. This effect is more prominent with increasing treatment time. The polar component contributed mostly to this effect, whereas the dispersion component did not show a significant contribution or changes after prolonged treatment. Silanisation of the acid-treated sample reduced the SFE to a value similar to that of the original untreated samples. However, the dispersion component displayed a marked contribution, nearly half of the total SFE. In addition to the polar carbonyl group, the dispersion contribution from the aliphatic methylene and vinylene groups of the acrylate moiety is responsible for these results.

Table 1: Surface free energy of water and glycerine probe liquids used during contact angle measurements, $a = 26$, $b = 27$.

Liquid	Total surface energy γ_1 (mJ/m ²)	Polar component (mJ/m ²)	γ_1^p	Dispersion component γ_1^d (mJ/m ²)
Water ^a	72.8	51		21.8
Ethylene glycol ^b	48.4	19.7		29.6

The angles made between the glass surface and the probe liquid are presented in Table 2.

Table 2: Contact angles between the glass surface and water and ethylene glycol.

Untreated sample	Treated sample	After acid treatment		After silanisation		
		Water	EG	Water	EG	
Water	EG					
48	50	After six hours acid treatment	36	39	45	42
		After 12 hours acid treatment	28	35	54	42

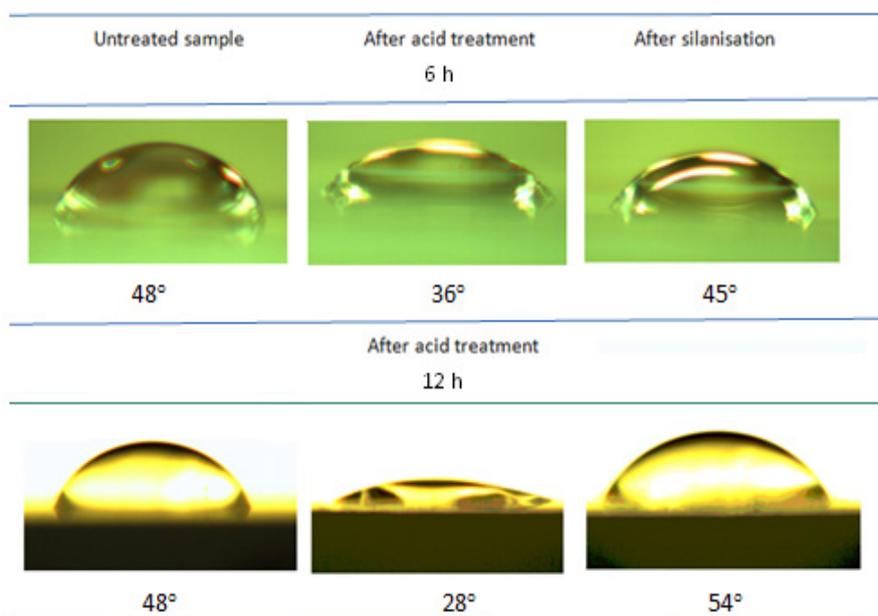


Figure 5: Changes in static contact angle of glass surface using water drop throughout modification stages after six hours and 12 hours.

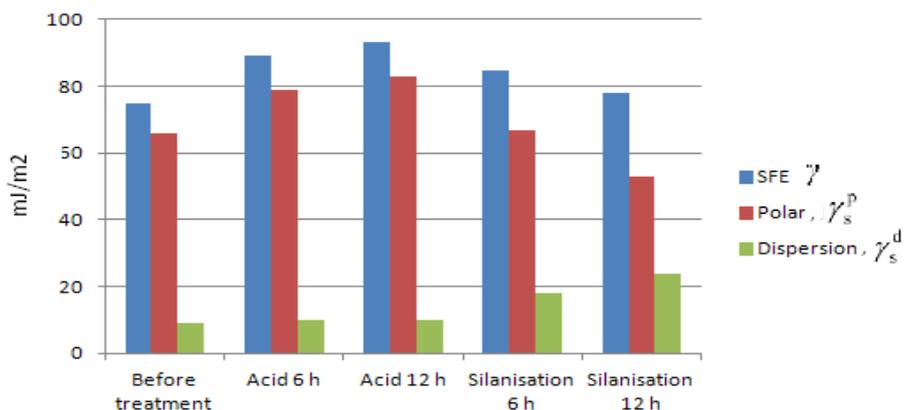


Figure 6: Changes in surface free energy of the glass surface under acid and silanisation treatments.

4. CONCLUSION

Surface modification of borosilicate glass covers was successfully achieved through the process of hydroxylation followed by silanisation. This process was established using ATR-FTIR spectroscopy, EDX analysis and static contact angle measurements. Hydroxylation under acid treatment induced the formation of silanol groups, whereas silanisation after grafting of TMSM onto the glass surface occurred via siloxane bonds. Hydroxylation is an equilibrium process, whereas prolonged acid treatment can affect the recondensation of the vicinal silanols to siloxane bridges. Hydroxylation induced hydrophilicity of the glass surface, which became more hydrophobic after silanisation with TMSM.

5. ACKNOWLEDGEMENTS

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