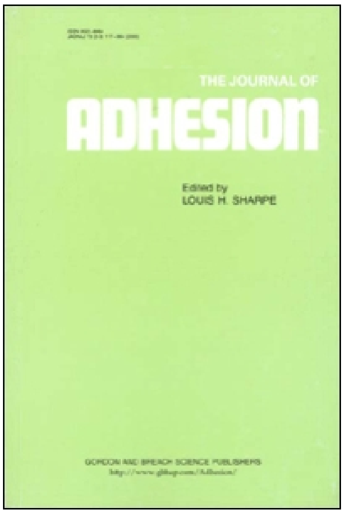

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In Situ FTIR Study of the Formation of an Organosilane Layer at the Silica/Solution Interface

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In Situ FTIR Study of the Formation of an Organosilane Layer at the Silica/Solution Interface*

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An FTIR experiment especially designed to study the growth of an organosilane layer at the interface between a solution and a *flat* silica surface is presented. High sensitivity is achieved by using the attenuated total reflection (ATR) technique in a liquid flow cell. The ATR crystal, either silicon or germanium, is covered with a very thin silica layer. Chemical reactions of a mono- and a di-hydrolyzable silane with the silica substrate have been investigated. The grafting of a submonolayer of the first reagent has been monitored by following the C—H and SiO—H vibrations. The density of grafted molecules has been estimated and information on the nature of the chemical bonding has been achieved. Evidence for the chain-polymerization of the dihydrolyzable silane at the substrate/solution interface has been inferred from the appearance of a Si—O—Si absorption band.

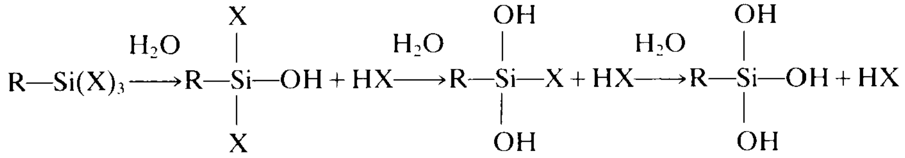
KEY WORDS organosilane; silica surface; surface reactivity; infrared spectroscopy; attenuated total reflection; interphase; chemical bonding; grafting.

INTRODUCTION

Organosilanes are widely used to improve the durability of adhesion between silicate glasses and polymers.[1] For this purpose, the surface of glass is commonly coated with an organosilane layer from an aqueous solution of a trihydrolyzable silane (general formula $RSiX_3$, where R is an appropriate organic group and X is a hydrolyzable group such as $—Cl$, $—OC_2H_5$, $—OCH_3$ . . .).

The silane deposition may be schematically represented as follows:[1]

The first reaction is the hydrolysis of the molecule:



$$\mathrm{R{-}Si(X)_3 \xrightarrow{H_2O} R{-}\overset{X}{\underset{X}{Si}}{-}OH + HX \xrightarrow{H_2O} R{-}\overset{OH}{\underset{OH}{Si}}{-}X + HX \xrightarrow{H_2O} R{-}\overset{OH}{\underset{OH}{Si}}{-}OH + HX} \qquad (1)$$

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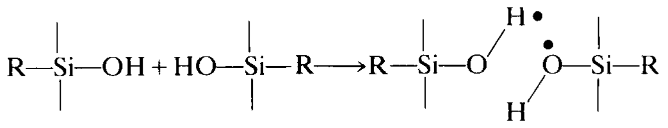
*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21-26, 1993.

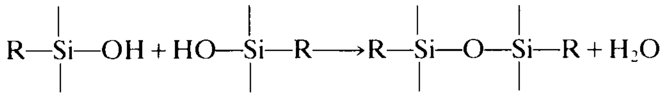
Further reactions occur competitively:

i) condensation of the hydrolyzed species in solution, via either hydrogen bonding (2) or covalent bonding (2′), leading to the formation of oligomers:



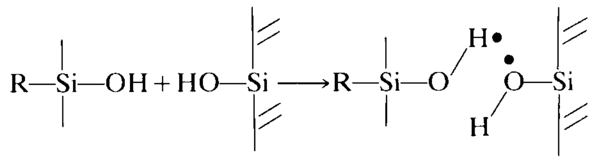
$$\mathrm{R{-}Si{-}OH + HO{-}Si{-}R \longrightarrow R{-}Si{-}O(H)\cdots O(H){-}Si{-}R} \tag{2}$$

or



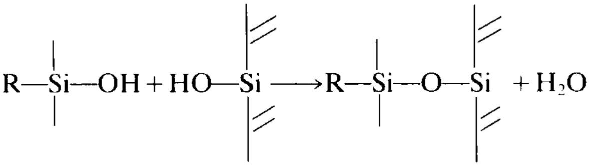
$$\mathrm{R{-}Si{-}OH + HO{-}Si{-}R \longrightarrow R{-}Si{-}O{-}Si{-}R + H_2O} \tag{2'}$$

ii) reaction of the hydrolyzed species with the silanol groups of the glass surface, via either hydrogen bonding (3) or covalent bonding (3′), leading to the grafting of a silane molecule:



$$\mathrm{R{-}Si{-}OH + HO{-}Si \longrightarrow R{-}Si{-}O(H)\cdots O(H){-}Si} \tag{3}$$

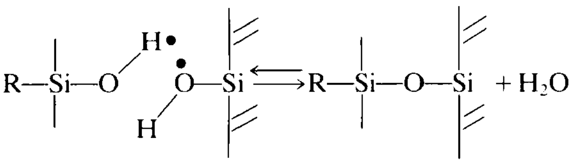
or



$$\mathrm{R{-}Si{-}OH + HO{-}Si \longrightarrow R{-}Si{-}O{-}Si + H_2O} \tag{3'}$$

The progressive growth of the organosilane layer occurs by condensation of hydrolyzed species (single molecules or oligomers in solution) onto previously grafted molecules via reactions (2) or (2′). This layer is a coupling medium which creates an interphase[2] between glass and polymeric materials.

Water plays a crucial role in the process. Plueddemann[1] has proposed a dynamic equilibrium at the interface:



$$\mathrm{R{-}Si{-}O(H)\cdots O(H){-}Si \rightleftarrows R{-}Si{-}O{-}Si + H_2O} \tag{3''}$$

Among the chemical reactions listed above, those occurring in solution—(1), (2) and (2′)—have been extensively studied and the relevant parameters (pH, concentration, etc. . .) are well identified.[3] On the contrary, reactions (3), (3′), (3″) and subsequent reactions of type (2) and (2′) at the surface are difficult to study. Previous experimental approaches have been mainly based on *ex-situ* analysis of the surface after treatment, with the exception of studies on the chemical reactivity of organosilanes with high specific area silica powders.[4] Besides the fact that the surface reactivity of a given material may vary with its specific area, flat substrates are of fundamental interest in adhesion science. Therefore, we have undertaken a specific program dedicated to the *in-situ* investigation of the role played by organosilanes at the interface between polymers and *flat* glass substrates.

Our first goal is to understand the formation of the organosilane layer at the substrate/solution interface. The experimental technique that we have used is infrared spectroscopy (FTIR). The major experimental problem of this technique is the poor signal-to-noise ratio due to the low specific area of flat surfaces. As shown in this paper, this problem can be overcome by using attenuated total reflection (ATR) at the surface of a well-defined crystal covered with a thin silica layer.

We report two preliminary experiments obtained with model systems: mono- and di-hydrolyzable silanes interacting with a pure silica substrate in an organic solvent. The results demonstrate the potential of this experimental approach and suggest that the method can be extended to the study of more complex systems such as those involved in the reinforcement of polymers with glass fibers.

EXPERIMENTAL PROCEDURE

Infrared Spectroscopy

A Nicolet 800 FTIR spectrometer equipped with a narrow-band mercury-cadmium-telluride detector has been used. Infrared spectra have been recorded at a resolution of 4 cm^{-1} with unpolarized light. All spectra have been obtained by coadding 128 interferograms. The ATR attachment is a beam-condensor from Harrick Scientific Corp. The optics includes spherical mirrors which maximize the total IR intensity available in the crystal. The liquid cell designed to fit the optics and to support the crystal uses Teflon® as the material in contact with the solution.

Substrates

The internal reflection elements (IRE) are $50 \times 10 \times 0.5$ mm^3, 45°, trapezoidal single crystals from silicon or germanium wafers. This geometry allows a total of one hundred internal reflections, but only 80 of them probe the solution inside the cavity of the flow cell. The transmission ranges are 8300–1500 cm^{-1} and 5500–700 cm^{-1}, respectively. In contrast with silicon, the germanium spectral window gives access to the Si—O—Si band at 1100 cm^{-1}.

In the case of silicon, the silica layer is native oxide, approximately 20 Å thick.[5] It has been prepared using the following chemical treatment of the crystal surface: H_2SO_4—H_2O_2 (10:1 by volume) at 120°C for 10 mins, deionized (DI) water rinse, HF—DI water (1:10 by volume) until hydrophobic, DI water rinse, DI water—H_2O_2—NH_4OH (5:1:1 by volume) at 80°C for 10 mins, Di water rinse, final drying in a N_2 gas stream.

On the germanium substrates, a SiO_2 thin film, typically 100 Å thick (measured by X-ray reflectivity), is deposited by RF sputtering using a silica target. Before deposition, substrates are cleaned using a trichloroethylene-acetone-methanol sequence for about 10 mins in an ultrasonic bath. The same procedure is used before each ATR experiment with a final UV/ozone treatment, for 1 hour each side.

Chemical Reagents

Triethylsilanol (TES), of chemical formula $(C_2H_5)_3SiOH$, and ethyldichlorosilane (EDCS), of chemical formula $C_2H_5(H)SiCl_2$, from Hüls-Petrarch, are used as reagents. Carbon tetrachloride (CCl_4) is used as the solvent because it does not present any strong absorption band in the wavenumber range of interest and has almost the same refractive index as amorphous silica. For some of the experiments, CCl_4 is dried over molecular sieves. The purity of the solvent is controlled by gas phase chromatography.

ATR-FTIR Experiments

To monitor the chemical conditions of the surface reaction, a peristaltic pump and a three-way valve are used to circulate either the pure solvent or the silane solution through the flow cell. The experimental set-up is maintained under a N_2 gas stream in order to avoid moisture. A fresh solution of silane in CCl_4 is prepared and checked by IR transmission spectroscopy. After preparation of the IRE, the flow cell is immediately assembled and aligned in the purged sample compartment of the spectrometer. A background spectrum is collected after the cell is filled with the solvent. Then, the silane solution is pumped into the cell. Spectra are collected during the reaction until no change can be detected. Finally, pure solvent is circulated through the cell to remove the molecules which have not reacted with the surface and spectra are collected, again until no change occurs.

RESULTS AND DISCUSSION

Grafting of a Submonolayer of a Monohydrolyzed Silane

Obviously, monohydrolyzable silanes cannot give rise to polymerization and their reaction with a silica surface can lead to the formation of, at most, one monolayer of grafted molecules. Therefore, these reagents permit one to study the nature of the chemical bonding with surface sites: reaction (3) or (3′). Moreover, they may serve as a way to evaluate the sensitivity of the experiment. To avoid any ambiguity about the hydrolyzed state of the reagent, we have chosen to work with TES which is pre-hydrolyzed and stable in solution. However, the surface reaction depends on many other physico-chemical parameters (such as surface hydration) that we have not systematically studied yet. The results presented here correspond to a particular experiment chosen to illustrate the very high sensitivity and the potential of this method with regard to chemical information. This experiment has been performed with a carefully-dried solvent.

Figure 1a shows the spectrum of the TES solution just before the ATR experiment. It has been obtained using a sealed transmission liquid cell with NaCl windows

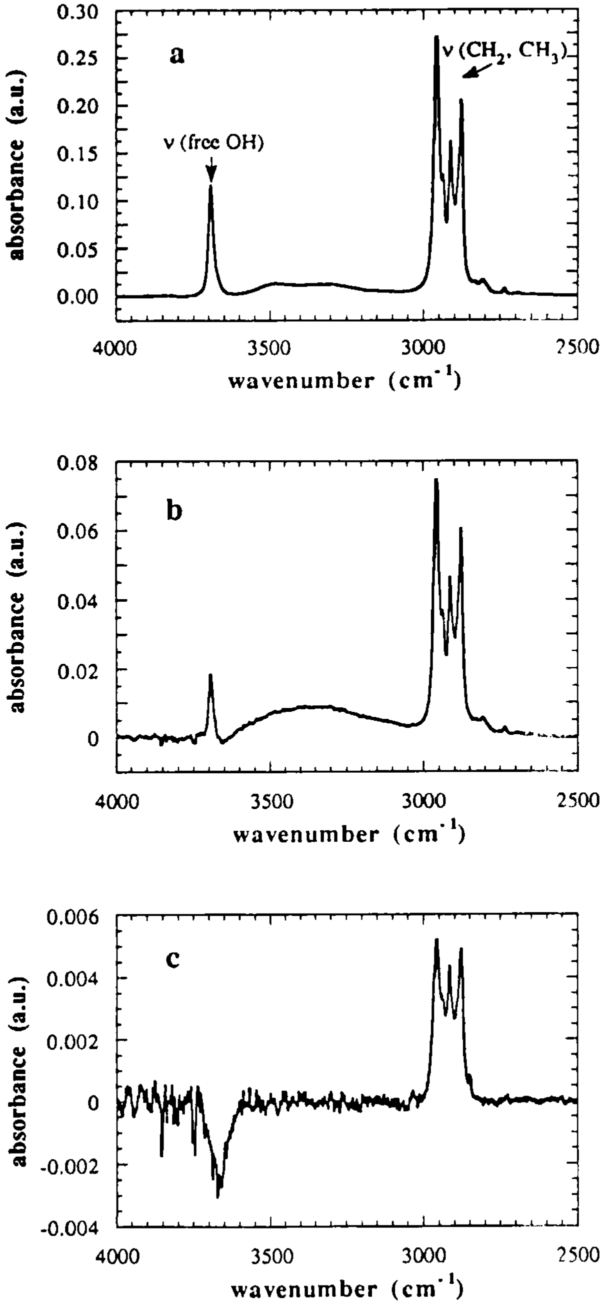


FIGURE 1 Infrared spectra in the O—H and C—H vibration region: a) transmission spectrum of the triethylsilanol reagent solution in carbon tetrachloride; b) attenuated total reflection spectrum in the liquid cell filled with the reagent solution at the end of the reaction; c) same as b) at the end of the rinsing with the pure solvent (note the vertical scale change).

(0.1 mm pathlength). The sharp absorption band of free O—H groups at 3693 cm^{-1}, together with the absence of any Si—O—Si band at 1100 cm^{-1}, confirm that TES is essentially stable in solution. The weakness of the IR absorption in the 3600–3200 cm^{-1} range is the indication that only a small part of TES interacts via hydrogen bonding. The C—H vibration spectrum can be decomposed into five bands. No attempt was made to assign all of them. We have focused on that of the high energy band which may be assigned to $\nu_{as}(CH_3)$ of the ethyl groups, as discussed by Rudakova and Pentin.[6] The C—H band was decomposed using Lorentz curves and the integrated absorbance of $\nu_{as}(CH_3)$ was calculated.

Figure 1b displays the spectrum obtained by ATR with a silicon IRE, when the cell is still filled with the TES solution (0.09 M) at the end of the reaction. In these conditions, the evanescent wave probes both the molecules grafted on the silica surface and those in solution. Evidence for the presence of the latter is the free O—H band. Compared with Figure 1a, we notice that: i) the intensity ratios of the CH_2 and CH_3 bands to the free O—H band are lower, ii) the bonded O—H band is broader and more intense. These two observations suggest that some of the molecules interact via hydrogen bonds.

The spectrum of Figure 1c has been obtained after rinsing with the reagent and leaving the pure solvent in the cell.The sharp band of the free O—H of triethylsilanols has completely vanished. This is also true for the bonded O—H band. Correlatively, the absorption of the CH_2 and CH_3 bands has significantly decreased. These changes result from the elimination of non-grafted single, and possibly dimer, molecules. Note that small changes in the width and the relative intensities of the different C—H bands has occurred, but the vibration frequencies are not modified.

The absence of any bonded O—H band after rinsing (3600–3200 cm^{-1} range) indicate that grafting has occurred via siloxane (Si—O—Si) bonds (reaction (3′)) and not via hydrogen bonding. As the characteristic Si—O—Si absorption band is outside the transmission window of silicon, it is not possible to detect directly the Si—O—Si bond with this IRE element. This could be achieved by using a germanium IRE, as in the case of the surface reaction of EDCS reported in the next section.

The downward band at 3665 cm^{-1} deserves special attention. It comes from species which disappear during the reaction. Its frequency corresponds to reactive surface silanols in a CCl_4 environment.[7] Thus, we assign it to the surface silanols which have reacted with reagent silanols to form a siloxane bond.

From the quantitative analysis of the intensities of the $\nu_{as}(CH_3)$ absorption band of spectra 1b and 1c, the amount of grafted molecules can be estimated.

Following Harrick[8] and Tompkins,[9] the absorbance of a band in an ATR spectrum is given by:

$$A = N\frac{n_2E_o^2}{n_1\cos\theta}\,\epsilon\int_0^\infty c(z)\exp(-2z/d_p)\,dz \qquad (4)$$

where N is the number of internal reflections, n_1 (respectively, n_2) the refractive index of the dense (respectively, rare) medium, E_o the electric field amplitude in the rare medium at the interface for unit incoming amplitude in the dense medium, θ the angle of incidence, ϵ the molecular extinction coefficient, d_p the penetration depth of the evanescent wave and c(z) the concentration profile of absorbing species in the rare medium. In our experiment, the absorbing species are the molecules in solution (concentration c_s, in cm^{-3}) and those grafted at the silica surface (surface concentration n_g, in cm^{-2}). Since the silica layer, of thickness t, and the solvent have the same index, n_2, the concentration profile can be written as:

$$c(z)=0 \quad \text{for } 0<z<t$$

and

$$c(z)=c_s+n_g\,\delta(z-t) \quad \text{for } z\geq t$$

where δ is the Dirac distribution.

Taking into account that $t \ll d_p$, equation (1) can be written:[10]

$$A=K(n_g+c_s\,d_p/2) \tag{5}$$

with

$$K=N\frac{n_2E_o^2}{n_1\cos\theta}\,\epsilon \tag{6}$$

Note that equation (5) lies on the assumption that ϵ is not modified by the grafting process, a point which will be discussed below.

Since K depends on E_o, two constants $K_\perp$ and $K_\parallel$ have to be considered in order to take into account the polarization of light. Therefore, we must write:

$$A_\perp=K_\perp\,(n_g+c_s\,d_p/2) \tag{7}$$

and

$$A_\parallel=K_\parallel\,(n_g+c_s\,d_p/2) \tag{8}$$

The $A_\perp$ (respectively, $A_\parallel$) absorbance could be measured if perpendicular (respectively, parallel) polarized light is used. The values of $K_\perp$ and $K_\parallel$ can be obtained from the $E_{o\perp}$ and $E_{o\parallel}$ values given in Reference 8.

The calculation of the absorbance, A_u, for non-polarized light, as a function of $A_\perp$ and $A_\parallel$, has been performed by Ohta and Iwamoto.[12] The general expression is quite complex, but it is easy to show that for a very weak absorbance ($A<0.05$), A_u is a linear function of $A_\perp$ and $A_\parallel$:

$$A_u=x\,A_\parallel+(1-x)\,A_\perp \tag{9}$$

where $x=I_{o\parallel}/(I_{o\parallel}+I_{o\perp})$ denotes the relative intensity of parallel-polarized incident light. From equations (6–8), we obtain:

$$A_u=[xK_\parallel+(1-x)\,K_\perp]\,(n_g+c_s\,d_p/2) \tag{10}$$

This expression shows that all unknown parameters (especially x and ϵ) can be ignored, provided that A_u is measured at different steps of the experiment. In the particular case of our experiment, we find that the ratio of the integrated absorbance of a given band recorded after the end of the reaction with reagents still in solution, $A_u(c_s \neq 0)$, to that of the same band recorded after having rinsed ungrafted molecules in the same solvent, $A_u(c_s = 0)$, is given by:

$$\frac{A_u(c_s \neq 0)}{A_u(c_s = 0)} = 1 + \frac{d_p c_s}{2\, n_g} \tag{11}$$

The experimental value of this ratio and the knowledge of d_p and c_s give access to n_g.

We have applied this method to the $\nu_{as}(CH_3)$ band of the ethyl groups of the reagent. In the frequency range of the C—H stretching mode for a 45° internal reflection between media of indices 3.4 and 1.4, d_p has a value of 275 nm. Consequently, the experimental data lead to $n_g \approx 0.65$ molecules/nm^2. It corresponds to one grafted molecule per 1.5 nm^2. This area is somewhat larger than that of about 0.6 nm^2 that may be evaluated with the van der Waals radii. This is compatible with the expectation that no more than one monolayer of ETS can be grafted on silica.

Further experiments will allow us to investigate the chemical reactivity of TES with surface silanols. However, a reliable estimation of the error on the n_g value will be necessary for quantitative studies. In fact, the calculation that we have presented here assumes: i) that the extinction coefficient is the same for the grafted molecules and those in solution, and ii) that the vibration modes of grafted molecules remain anisotropic. Although quantitative arguments are still missing, we feel that this approximation is roughly justified in the case of the $\nu_{as}(CH_3)$ band for the following reasons. Firstly, the frequency of the absorption maximum is not modified at all (2959 cm^{-1} for spectra 1b and 1c). Secondly, according to simple stereochemical considerations on the molecule and the large number ($3 \times 3 = 9$) of $\nu_{as}(CH_3)$ vibrators per molecule, these vibrators should not be far from being randomly distributed, on average.

Polymerization of a Dihydrolyzable Silane at the Silica/Solution Interface

Dihydrolyzable silanes can only give rise to chain polymerization. As an example, we have studied the reaction of EDCS at a silica surface. This particular reagent has been chosen because of the high reactivity of Cl groups and the rich potential of information that can be obtained from the Si—H infrared band. The polymerization can be observed with the time evolution of both this Si—H band and the Si—O—Si band at 1100 cm^{-1}. To detect the latter, a germanium crystal is used as the IRE. Again, carbon tetrachloride has been used as the solvent, but it has not been dried in order to bring the water necessary for the hydrolysis of the reagent at the interface.

The transmission spectrum of the reagent in a CCl_4 solution (0.09 M) is shown in Figures 2a and 3a for the Si—H and Si—O—Si regions, respectively. The band at 2206 cm^{-1} corresponds to the Si—H stretching band. CH_2 wagging and rocking modes, C—C deformation and CH_3 wagging and rocking modes account for the 1230 cm^{-1}, 1013 cm^{-1} and 967 cm^{-1} bands, respectively. Evidence for a small amount of condensation due to residual water in the solvent is given by the detection of the Si—O—Si absorption band around 1100 cm^{-1}. Figures 2b and 3b display the spectrum of the same reagent in CCl_4 with a small amount of water intentionally added. In this case, a pronounced condensation occurs (reaction (2′)). It gives rise to a huge increase of the Si—O—Si band intensity and to a shift of the Si—H band. Thus, the 2161 cm^{-1} band can be assigned to Si—H bonds of molecules condensed via siloxane bonding. This shift toward low frequency is due to the inductive power of substituents of different electronegativities on the silicon atom.[13]

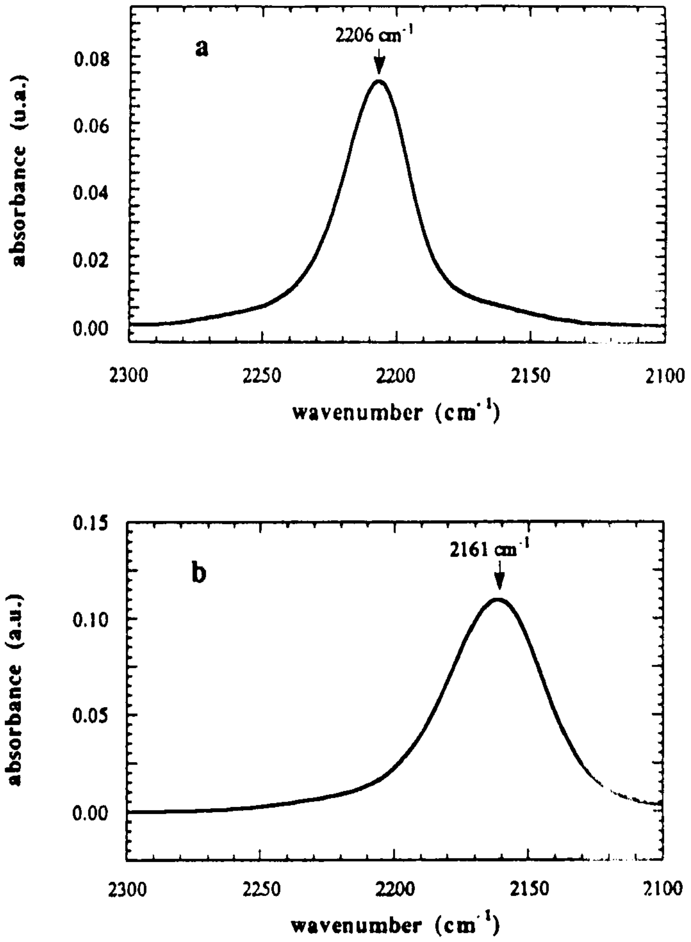


FIGURE 2 Infrared spectra in the Si—H vibration region: a) transmission spectrum of the ethyldichlorosilane reagent solution in carbon tetrachloride; b) same as a) when a small amount of water is added to the solution; c) attenuated total reflection spectrum in the liquid cell filled with the reagent solution at the end of the reaction; d) same as c) at the end of rinsing with the pure solvent.

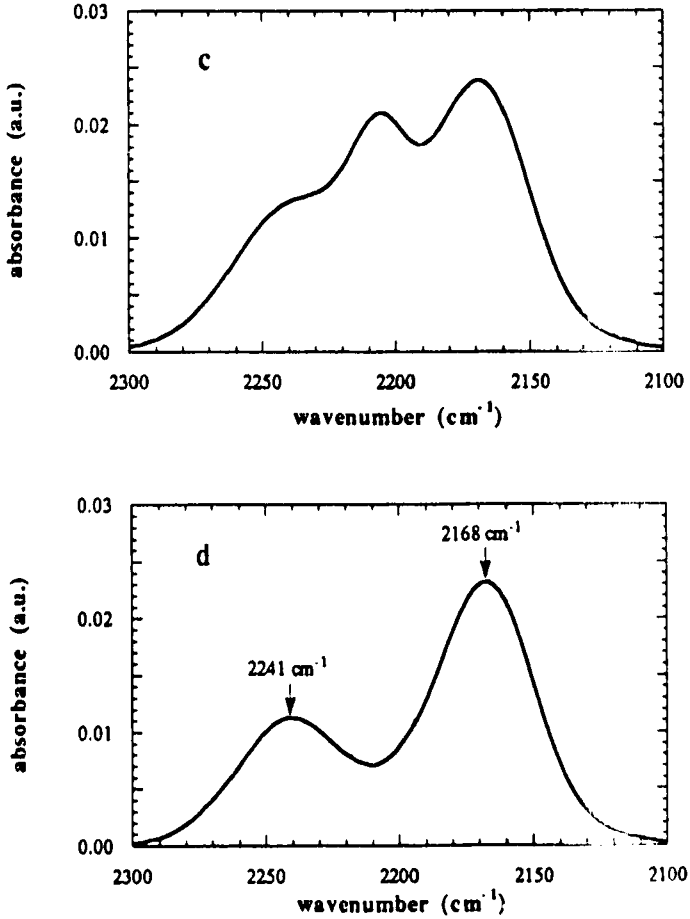


FIGURE 2 *(Continued)*

Figures 2c and 3c display the ATR spectrum obtained at the end of the reaction when the cell is filled with the silane solution (0.09 M). As in the case of Figure 1b, the evanescent wave probes both the grafted molecules and those in solution. Some polycondensation has developed, as can be seen from the high intensity of the Si—O—Si band and from the presence of a Si—H band at 2168 cm^{-1}. A third Si—H absorption band near 2240 cm^{-1} is also observed.

The spectrum shown in Figures 2d and 3d has been obtained after having rinsed the reagent with the pure solvent. The removal of reagent molecules in solution is confirmed by the vanishing of the 2206 cm^{-1} Si—H band. The fact that no significant difference appears in the Si—O—Si region indicates that almost all the condensed molecules belong to polymerized chains grafted on the silica surface. From the intensity of the CH_2 band (not shown here), we can apply the same quantitative analysis as the one described in the previous section. Here, we obtain $n_g \approx 8$ nm^{-2} for the concentration of grafted EDCS units.

The set of results reported above does not allow us to propose a complete description of the structure and the chemical organization of the grafted layer. Nevertheless, semi-quantitative information can be obtained if we postulate that each polymerized chain needs at least one surface site to be bonded to. From the n_g value given above and a rough approximation of 1 nm^{-2} for the density of surface sites, we can estimate the mean length of the chains to be of the order of 10 monomer units. The conformation of these chains at the silica/solvent interface remains an open question. A more extensive study of the Si—H vibration at 2241 cm^{-1} could give relevant information on this matter. However, we cannot exclude the possibility that this band comes from other Si—H bearing molecules, traces of which may be in the reagent, which would strongly react with the silica surface.

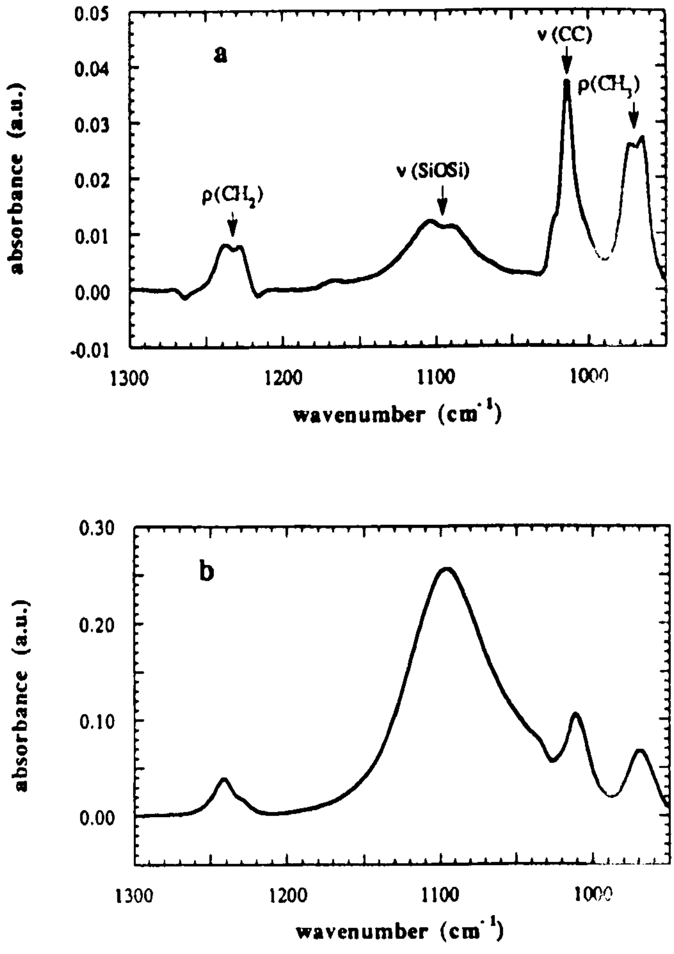


FIGURE 3 Same as Fig. 2, in the Si—O—Si vibration region.

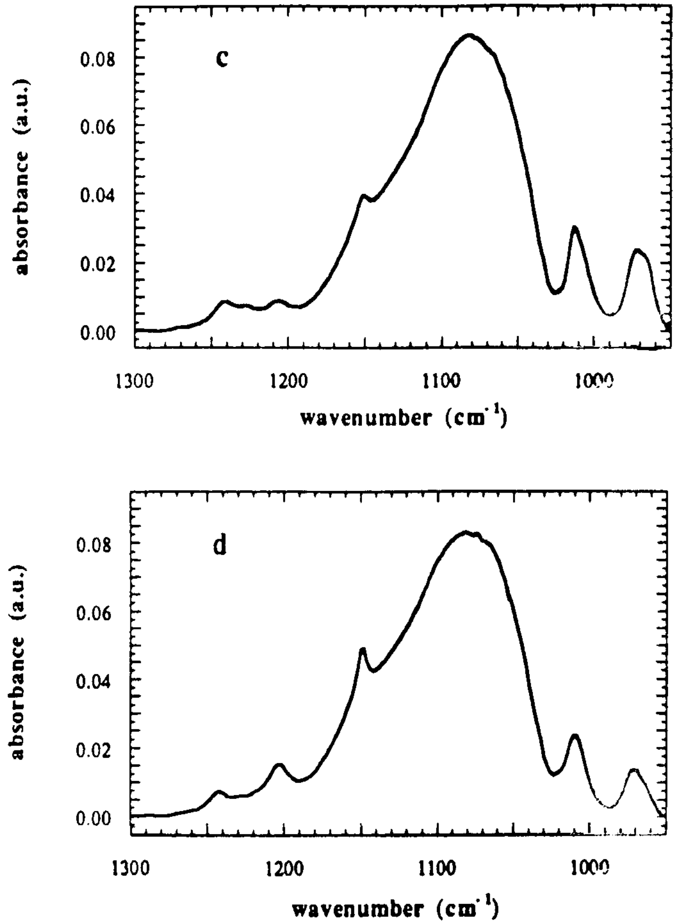


FIGURE 3 *(Continued)*

CONCLUSION

We have shown that a comprehensive experimental study of organosilanes reactions at flat silica surfaces is possible using FTIR spectroscopy provided that, i) experiments are made by means of attenuated total reflection (ATR) to achieve a high sensitivity, ii) experiments are performed *in situ,* using a liquid flow cell, and iii) a germanium crystal covered with a silica thin film is used, allowing a direct observation of the siloxane bonds.

Under these conditions, it is possible to identify the nature of the chemical bonds involved in the grafting of molecules, even at the submonolayer level. This opens the way to a detailed investigation of the structural and chemical organization of the grafted layer, as demonstrated in this paper for the particular case of one mono- and one di-hydrolyzable silane. The study of the formation of a three-dimensional crosslinked layer built with a trihydrolyzable silane is in progress.

The method can be extended to any organosilane, including alkoxysilanes, to other solvents and to other substrate materials, provided that they can be deposited as a thin film on the IRE surface. Experiments with alkoxysilanes in aqueous solution and germanium IRE coated with glass have started in our laboratory. Other interphases, such as silica/polymer, can also be probed using this approach.

Acknowledgements

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