

## Monomolecular silane films on glass surfaces—contact angle measurements

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### Abstract

Contact angle measurements have been done for silanized glass plates with 11 different coatings. For a monomolecular film of tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilyl groups on a glass surface, contact angles (water 24°C) have been measured to  $\theta_s = 111^\circ$ ,  $\theta_l = 99^\circ$ . The figures are comparable with those obtained for bulk Teflon, but with smaller hysteresis behaviour. The silanes are believed to form chemically anchored monomolecular films with a densest array of aliphatic side chains. MM2 calculations for model compounds reveal significant attractive van der Waals forces between the aliphatic chains, which can be seen as a driving force for a 2D self-assembly on the surface. This high state of order is assumed to play a crucial role for optimum hydrophobization. Furthermore, photochemical crosslinking has been done with films of 7-oct-1-enyltrimethoxysilane to increase the wear resistance of the coatings. © 1997 Elsevier Science S.A.

### 1. Introduction

In a country like Singapore with an annual rainfall as high as 4000 mm, objects continuously exposed to extremely wet conditions suffer considerable loss of value due to rapid degradation. It is economically advisable to invest in protective measures such as appropriate hydrophobization of surfaces.

To make a surface hydrophobic it is necessary to reduce long-range attractive forces, e.g. coulombic or electrostatic interactions, hydrogen bonding, dipole interactions, solvation effects or van der Waals forces [1]. Our strategy involves chemical attachment of a monomolecular layer of a strongly hydrophobic material (for instance a film containing fluorinated chains) through a silyl ester anchor group. As a specimen, glass plates are used to allow a standardized coating process. The silanes are covalently bonded to the glass surface by a coupling and a curing process. In some cases, a further photochemical crosslinking step is involved [2]. The applied silanes generally contain an aliphatic side chain as protecting group. The side chains are assumed

to self-assemble to a two-dimensional (2D), highly ordered densest packed array on the surface [3]. Our investigations compare a variety of aliphatic and olefinic chain-silanes, including those with fluorinated end groups.

A thermodynamic parameter related to the hydrophobicity of a surface is its surface tension. However, the surface tension  $\gamma_{SV}$  at a solid–vapour interface is difficult to measure directly. For the sake of convenience, contact angles, e.g. between a drop of water and the surface, are commonly used as an indicator for the surface properties [4]. The contact angle  $\theta$  is defined as the angle formed by two planes tangential to the liquid and solid surfaces at the site of contact between the two phases and the surrounding phase (Fig. 1).

A relationship between contact angles and surface tension is provided by Young's equation (Eq. (1)). According to Eq. (1), the contact angle of a drop of liquid on a solid surface, where the solid, liquid and vapour phases are in equilibrium, is given by

$$\gamma_{SV} - \gamma_{LS} = \gamma_{LV} \cos \theta_{LSV} \quad (1)$$

where  $\gamma_{SV}$ ,  $\gamma_{LS}$ ,  $\gamma_{LV}$  are the interfacial tensions at the solid–vapour, liquid–solid, liquid–vapour interfaces respectively, and the subscript LSV denotes the solid–liquid–vapour interface. A solid is defined to be completely wetted by a liquid when  $\theta = 0^\circ$ , partially wetted

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<sup>2</sup> See footnote 1.

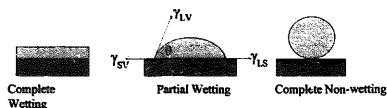


Fig. 1. Contact angle and surface tension.

when  $0 < \theta < 180^\circ$ , and non-wetted when  $\theta = 180^\circ$ . However, a surface is generally considered hydrophobic when  $\theta > 90^\circ$ .

A rational organization of contact angle data has been made by Zisman plots [5]. For a homologous series of liquids on a given surface, such as Teflon,  $\cos \theta$  is plotted as a function of  $\gamma_{LV}$ . This graph normally represents a monotonic function, and its extrapolation to zero  $\theta$  provides the critical surface tension  $\gamma_c$  which can be taken as a quantitative characteristic of the solid–liquid–vapour interface ( $\gamma_{SLV}$ ). The interrelation between  $\gamma_{SLV}$  and  $\theta_{SLV}$  is then given by  $\cos \theta_{SLV} = 1 - \beta(\gamma_{LV} - \gamma_c)$  (2)

$\beta$  usually has a value of about 0.03–0.04. Eq. (2) allows one to calculate contact angles. It should be noted, however, that Zisman plots for silylated glass surfaces rarely show a linear relationship; this is caused by different dispersive and polar components of the surface tension  $\gamma_{LV}$  [5].

## 2. Experimental

### 2.1. Preparation of glass plates

Glass plates were cleaned with chromic acid and purified with deionized and distilled water and finally dried at  $200^\circ\text{C}$  for 12 h to remove traces of water. The plates were stored under anhydrous conditions prior to use.

### 2.2. Coating

The coatings were applied from a solution of dry  $\text{CH}_2\text{Cl}_2$  (distilled from  $\text{P}_2\text{O}_5$  prior to use) as 70 mol%, 50 mol% and 25 mol% solutions of the silanes. One set of plates was also coated with pure silanes. In all cases, three glass plates were each dipped into the coating agent for either 30 s, 1 min or 2 min. The plates were stored in an Ar atmosphere at  $24^\circ\text{C}$  for 24 h, rinsed in a  $\text{CH}_2\text{Cl}_2$  bath and heated to  $120^\circ\text{C}$  for 3.5 h. The plates were washed a second time with  $\text{CH}_2\text{Cl}_2$ , dried at  $50^\circ\text{C}$  (20 min) and stored in an Ar atmosphere.

### 2.3. Contact angle measurements

The advancing angle of a sessile drop of liquid was measured directly through a comparator microscope

fitted with a goniometer scale. As contact angles are known to vary with the size of the liquid drop, time and temperature, all measurements were taken in a room at a constant temperature of  $24^\circ\text{C}$ . The size of the liquid drop was controlled by the micrometer syringe and approximately the same time was taken for each measurement. The receding angle was measured by extracting a fixed amount of the liquid from the drop on the glass plate with the syringe. Readings were also taken on different parts of the coated plate for both the advancing and receding angles and an average of the values (correct to the nearest degree) was calculated. In the case of the three plates coated with the same reagent, an average of all the contact angles measured was taken. To give an indication of the accuracy of the measurements, the standard deviations were calculated.<sup>3</sup>

### 2.4. Photochemical crosslinking

Plates coated with 7-oct-1-enyltrimethoxysilane, allyltriethoxysilane and vinyltriethoxysilane were subjected to photolysis in a Rayonett photoreactor equipped with low pressure Hg lamps of monochromatic light of 254 nm. Analysis of the plates was done by reflective IR spectroscopy.

### 2.5. Durability test

The silane-coated plates were immersed into deionized water for 1 week before contact angle measurements were retaken. This procedure was repeated.

## 3. Results and discussion

The coating process included a variety of chain silanes, as well as silanes with fluorinated end groups and with incorporated double bonds. The latter were chosen to study crosslinking reactions of the anchored species. The monomolecular films were attached to the surface by a condensation reaction with the silanol groups of the glass. To ensure complete coverage, a curing process has been done [6]. Any excess of unreacted silanes was removed. In the ideal case the alkyl-chains form a densest 2D packing giving rise to the formation of a monomolecular film with liquid crystalline properties. The formation of monomolecular films by this procedure has been established in the literature: fluorinated silica gels are commercially available [7]. Contact angles are measured both as advancing and receding angles. Both values undergo a hysteresis be-

<sup>3</sup> Tables available from the author upon request.



Fig. 2. Definition of advancing  $\theta_a$  and receding  $\theta_r$  contact angles.

behaviour with  $\theta_r < \theta < \theta_a$  (Fig. 2). A clean glass plate was measured to  $\theta_a = 76^\circ$  and  $\theta_r = 74^\circ$  with low hysteresis. The hysteresis behaviour is a reflection of surface roughness and heterogeneity.

A comparison of the contact angles for various silane coatings (Fig. 3) shows particularly high values for chlorosilanes. We interpret this effect in the sense of a higher reactivity of halosilanes compared to alkoxy-silanes resulting in a more efficient coverage of the surface. However, practical applications of halosilanes are limited due to their reactivity and HCl elimination. In the series of the ethoxysilane-coating reagents, clearly the fluorinated species tridecafluoro-1,1,2,2-tetrahydro-octyl-1-triethoxysilane, where  $\theta_a = 111^\circ$  and  $\theta_r = 99^\circ$  are found, forms the most hydrophobic films. The values of the monomolecular film are almost identical to a poly-tetrafluoroethylene (Teflon) surface for which  $\theta_a = 112^\circ$  and  $\theta_r = 95^\circ$  have been measured [8]. (Calculation according to Eq. (2) yields a contact angle of  $131^\circ$  for a Teflon surface.) The hysteresis behaviour has been found to be much smaller for the film than for the bulk polymer, indicating a very even film on the glass surface in the sense of a monomolecular layer. It is also remarkable that contact angle values show a relatively small standard deviation, which is in line with highly uniform coatings.

If excess coating agent is not removed properly, contact angles of the films are generally lower. This is ascribed to the formation of multilayer films with a less ordered surface, resulting in an increase of surface tension.

A particularly interesting system is that for a film of tetraethoxysilane, which yields a contact angle as high as  $141^\circ$ . It seems to be that a particular hydrophobic modification of  $\text{SiO}_2$  coating is formed, but experiments with  $(\text{EtO})_3\text{Si}$  have not been pursued due to the high standard deviations of the measurements.

The quality of the coatings is also a function of the exposure time. Experiments with tridecafluoro-1,1,2,2-tetrahydro-octyl-1-triethoxysilane, *n*-dodecyltriethoxysilane and vinyltriethoxysilane (in  $\text{CH}_2\text{Cl}_2$ ) showed an optimum coating time of the glass plates of 30 s. Prolonged exposure to the silane solution did not increase contact angles, but rather led to a reduction of contact angle. This effect is assumed to occur from disordered multilayers. With allyltriethoxysilane the optimum time of exposure was 2 min, suggesting a more sluggish coupling reaction.

A test for wear resistance has been done by long term exposure of the films to water (3 weeks) (Fig. 3). The contact angles were virtually constant in the case of tridecafluoro-1,1,2,2-tetrahydro-octyl-1-siloxy coatings. In other cases a slight decrease was monitored in the first week, with the values stabilizing after the second week. In some cases, even an increase of contact angle is registered after 1 week exposure to water. In those cases it is assumed that the surface was covered with residual coupling agent. The data clearly support our argument that, in particular, monomolecular films display the highest contact angles, because an optimum organization of the surface is achieved.

Molecular modelling calculations with the MM2 force field indicate significant attractive van der Waals forces between tridecafluoro-1,1,2,2-tetrahydrooctyl side chains. Calculations for the simple disilylester  $(\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OH})_2)_2\text{O}$  reveal attractive (non-1,4-van-der-Waals interactions) of  $-8.6 \text{ kcal mol}^{-1}$  between the two aliphatic chains as source for the formation of a *cis*-isomer as ground state. A more realistic model for a surface is given with the trisilylester  $(\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OH})_2)_3\text{O}$  (A (Fig. 4(a,b)) and the tetrasilylester  $(\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OH})_2)_4\text{OSi}(\text{OH})_2(\text{CH}_2)_2(\text{CF}_2)_5\text{CF}_3$  B (Fig. 4(c,d)). For A, the conformer with all three side chains in a parallel arrangement appears to be  $11.0 \text{ kcal mol}^{-1}$  lower in total energy than its bent conformer which does not allow significant interactions between the fluorinated side chains. After 1000 cycles of iterations, the following energies are obtained (parallel/bent conformer):  $E_{\text{tot}} = 234.7/245.3$ ,  $E_{\text{str}} = 29.3/29.7$ ,  $E_{\text{b}} = 19.20/19.7$ ,  $E_{\text{sb}} = 3.3/3.4$ ,  $E_{\text{tors}} = -61.6/-60.8$ ,  $E_{1,4\text{-VDW}} = 12.5/12.3 \text{ kcal mol}^{-1}$ ,  $E_{\text{non-1,4-VDW}} = -16.5/-5.8 \text{ kcal mol}^{-1}$ . The energetic differences between both conformers can predominantly be ascribed to differences in stretching/bending energies and differences in attractive van der Waals forces. Attachment of a further silylester as side chain to the six-membered siloxy ring also yields a slight energetic preference of 2.1 kcal mol<sup>-1</sup> for the *all-cis*-rotamer with a nearly parallel arrangement of the aliphatic chains (*cis*-rotamer/*trans*-rotamer, 1500 iterations, B:  $E_{\text{tot}} = 308.0/310.1$ ,  $E_{\text{str}} = 36.6/38.6$ ,  $E_{\text{b}} = 23.7/23.1$ ,  $E_{\text{sb}} = 4.5/4.6$ ,  $E_{\text{tors}} = -81.1/-82.6$ ,  $E_{1,4\text{-VDW}} = 16.7/15.9 \text{ kcal mol}^{-1}$ ,  $E_{\text{non-1,4-VDW}} = -21.7/-16.5 \text{ kcal mol}^{-1}$ ). These results underline the importance of attractive van der Waals forces for the self-assembly of monomolecular organosilane films.

The ultraviolet treatment of films formed by 7-oct-1-enyltrimethoxysilane, allyltriethoxysilane and vinyltriethoxysilane did not affect contact angles very much, but led to an increase in wear resistance of the coatings. Crosslinking of the 7-oct-1-enyltrimethoxy side groups was proven by reflective IR spectroscopy indicating a decrease in intensity for the  $\nu\text{C}=\text{CH}$  mode at

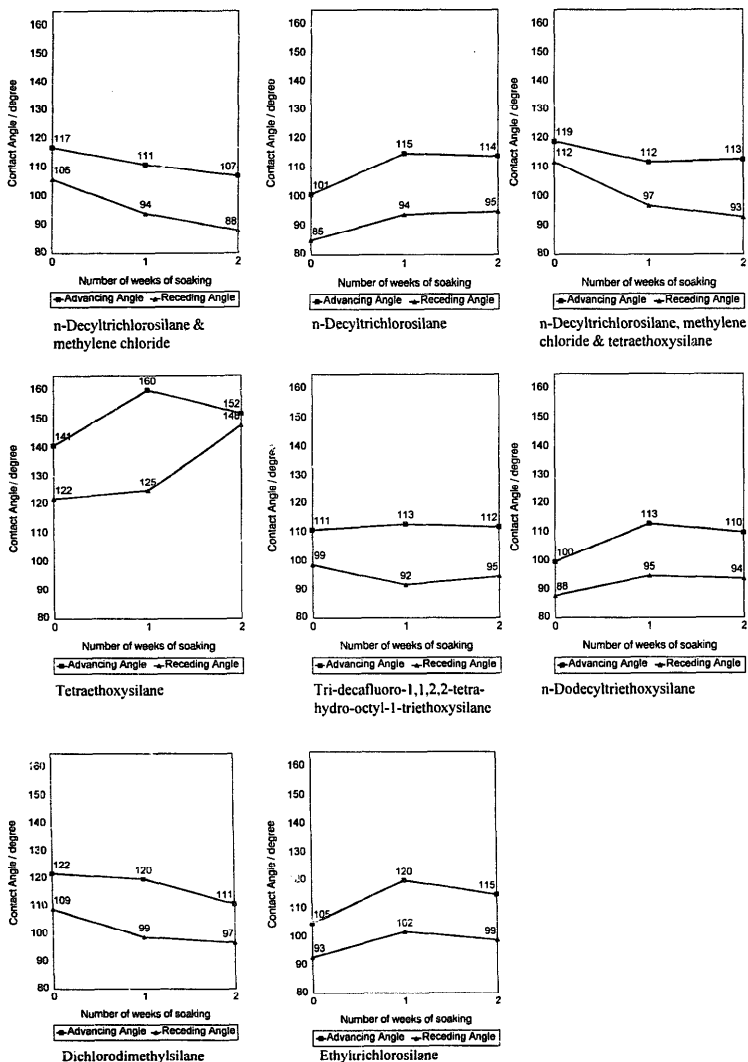


Fig. 3. Contact angles as a function of exposure time to water.

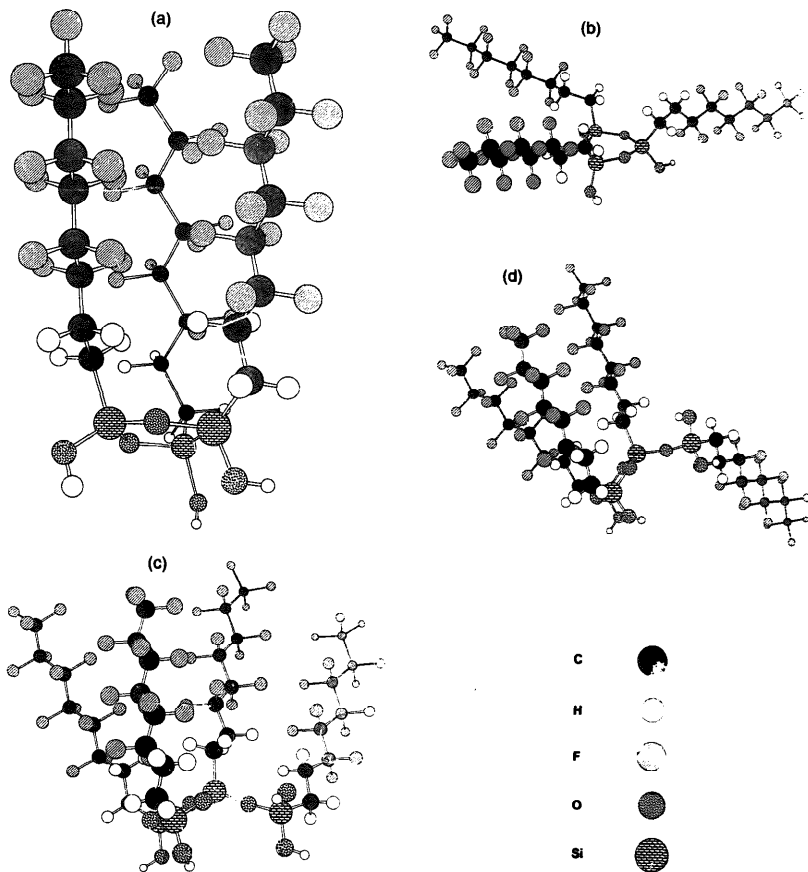


Fig. 4. Calculated conformations (MM2) for  $[C_6F_{13}CH_2CH_2Si(OH)O]_3$ : A: the all-cis conformer (a) is  $11.0 \text{ kcal mol}^{-1}$  lower in energy than the trans-conformer (b). MM2 calculation for  $[C_6F_{13}CH_2CH_2Si(OH)O]_2OSi(OH)_2(CH_2CH_2C_6F_{13})_3$ : B: the all-cis conformer (c) is  $2.1 \text{ kcal mol}^{-1}$  lower in energy than the trans-conformer (d).

$1646.7 \text{ cm}^{-1}$ . Furthermore, a second IR absorption at  $1652.5 \text{ cm}^{-1}$  occurred after 245 nm photolysis of the plates, indicating some degree of cis–trans isomerization of the double bonds. Crosslinking is supposed to occur by (2 + 2) cycloaddition reaction of neighbouring olefinic units. Such a process connects the side chains pairwise. A further indicative peak appeared at  $788 \text{ cm}^{-1}$  typical for siloxane bonds on a glass surface [9].

#### 4. Conclusions

Chemical coupling of alkyl and alkenylsilanes to glass (silica) surfaces leads to a remarkable increase in hydrophobicity. As expected, the fluorinated trisdecylfluoro-1,1,2,2-tetrahydro-octyl-1-tri-ethoxysilane yields films with contact angles higher than those from most other coatings with non-fluorinated side-groups. The

measured contact angles (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane  $\theta_s = 111^\circ$ ,  $\theta_a = 99^\circ$ ) are almost identical to those known for the system water-poly-tetrafluoroethylene (Teflon),<sup>4</sup> but with a much smaller hysteresis. Arguments based on both stoichiometry and the low hysteresis behaviour of the contact angles suggest the presence of a uniform, monomolecular film. It is the high state of order in these layers which causes favourable contact angle properties. The long-term stability of the samples is remarkable; this is related to the rigorous chemical bonding of the films to the surface. The high hydrophobicity of fluorinated surfaces is known and can be correlated to the large van der Waals radii of the fluorinated end groups of the side chains which form a most effective hydrophobic shield on the surface. The films presumably achieve a liquid crystalline state by self-organization, which seems to be crucial for optimum hydrophobization. As result of an MM2 force field calculation for a molecular model compound, particularly attractive van der Waals forces favour the self-assembly of the alkyl side chains to a highly organized film. A detailed study of the monomolecular surface phase by more advanced methods, such as ellipsometry, is the subject of a current research project [10].

Monomolecular films represent an optimum with respect to costs, performance and wear resistance. A further important point with view to applications is the given oxygen-permeability of silane-coated surfaces, which is, in concert with its hydrophobicity, an important requirement for the appropriate protection of buildings.

<sup>4</sup> Regular pTFE which has not been subjected to a special curing process. (Curing results in reduction of surface roughness and an increase of contact angles.)

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