

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

The diagram illustrates various silane coupling agents used in the synthesis of hybrid materials. The structures are defined as follows:

- Top structure:** A linear silane with two  $Rf$  groups and a central  $Si-O-Si-O-Si$  core.
- Middle structure:** A branched silane with three  $Rf$  groups and a central  $Si-O-Si-O-Si$  core.
- Bottom structure:** A silane with two  $Rf$  groups and a central  $Si-O-Si-O-Si$  core.

The structures are labeled with  $Rf$  groups and  $Si-O-Si-O-Si$  cores.

RSC Advances Accepted Manuscript

## ARTICLE

# Effect of the Type of Fluorofunctional Organosilicon Compounds and the Way of Their Application onto the Surface on its Hydrophobic Properties.

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

H. Maciejewski<sup>a,b,†</sup>, J. Karasiewicz<sup>b</sup>, M. Dutkiewicz<sup>c</sup>, M. Nowicki<sup>d</sup>, and Ł. Majchrzycki<sup>c</sup>

Fluorofunctional silanes, polysiloxanes and silsesquioxanes have been employed for the modification of glass surface in order to determine their influence on hydrophobic properties. Moreover, to increase hydrophobicity of the surface, the modification was performed in two stages: (i) by pretreatment with the use of silica sol (a rise in the surface roughness), (ii) modification with the above silicon compounds. The measure of hydrophobicity is the contact angle determined by drop profile tensiometry. The examined fluorocarbofunctional organosilicon derivatives are good precursors for the synthesis of highly hydrophobic materials and coatings. In some cases the values of contact angles measured after the surface modification exceeded 150°, i.e. they fell in the range characteristic of superhydrophobic surfaces.

## Introduction

Non-wettable surfaces with high water contact angles (WCA) have received tremendous attention in recent years<sup>1</sup>. Superhydrophobic coatings, i.e. those with WCA > 150°, have found many spectacular applications based, in particular, on their self-cleaning<sup>2</sup>, anti-icing<sup>3, 4</sup>, oil repellent<sup>5</sup>, electrowetting<sup>6</sup> and anticorrosive<sup>7</sup> activities. The wettability of a surface depends on two factors: (i) its chemical composition and (ii) its structure (roughness). Different techniques of producing rough surfaces were developed by the imitation of nature (biomimetics), namely such ones as wet chemical etching<sup>8, 9</sup>, inorganic or organic template method<sup>10</sup>, electrospinning<sup>11</sup>, phase separation<sup>12</sup> and colloidal self-assembly<sup>13, 14</sup>. In particular, the latter is very popular because the production and application of particles and nanoparticles on a surface makes it possible to easy control its roughness<sup>15-17</sup>. One of ways to achieve this goal is the use of different particle size silica that is obtained in the sol-gel process. The mild preparation conditions offer the possibility of incorporating a wide range of labile organic species into a glass composite. Moreover, sol-gel derived

materials exhibit tunable porosity, transparency, hardness and good thermal stability<sup>18-24</sup>.

In the case of chemical modification, the most efficient are fluorine-containing compounds<sup>25, 26</sup>. In particular, the best effect is obtained by applying fluoro derivatives of organosilicon compounds which combine unique properties of the both components<sup>27</sup>. From among this group of compounds fluorofunctional trichloro- and trialkoxysilanes<sup>28-30</sup>, as well as fluorosilicones<sup>27, 31, 32</sup> were applied most often, and recently also fluorofunctional silsesquioxanes<sup>33-35</sup> found their application. Functional silsesquioxanes due to their unique properties, e.g. the rigid nanoscale silicon-oxygen core with a diameter of about 1.5 nm, are often regarded as the smallest silica particle that can also influence the surface roughness and tunable properties of functional groups attached to silicon atoms. This is why the fluorofunctional silsesquioxanes are good precursors for the synthesis of highly hydrophobic materials.

In spite of many interesting properties, fluorofunctional silicon compounds are not commonly applied to this purpose mainly because of difficulties in their synthesis, high price and poor

availability of raw products. Our many years' standing studies of the process of hydrosilylation of different olefins enabled to develop effective catalysts for the process<sup>36</sup>, including fluorinated olefins. Due to this, it was possible to perform simple syntheses of fluorofunctional silanes, polysiloxanes and silsesquioxanes as a one-pot process<sup>37-39</sup> and to use them later for the surface modification. However, fluorocarbofunctional groups, in spite of their specific properties, surface properties in particular, are not reactive from the chemical point of view. To create a stable bond to a substrate, the presence of another reactive group is necessary, as it is the case of fluorofunctional trialkoxysilanes. This is why we developed a method of synthesis (based on consecutive hydrosilylation of two different olefins) of polysiloxanes and silsesquioxanes containing, besides fluoroalkyl group, also trimethoxysilyl or glycidyl group<sup>40</sup>. The latter makes it possible, through the reaction with hydroxyl groups present on the surface, to stably bond them to a substrate.

In most papers on hydrophobic properties, results are presented for the effect of only one type of organosilicon derivative, while there are no reports on the comparison of the effect of different types of silicon compounds. For this reason we present in this paper results of our research on the modification of glass surfaces with the use of fluorofunctional silanes, polysiloxanes and silsesquioxanes containing also the mentioned reactive groups. In addition to octafluoropentyloxypropyltrimethoxysilane, we have used in our study also two siloxane copolymers of the same length of siloxane chain and the same number of octafluoropentyloxypropyl groups, however differing in the type of reactive groups (trimethoxysilylethyl or glycidoxypropyl ones), as well as two silsesquioxanes (POSS) with the analogous type of groups. The choice of such derivatives was based on results of our earlier studies. Moreover, the present study was aimed at determining the effect of the modification way on the developed hydrophobic properties of the substrate. To meet this aim, modifications were performed by using solutions of organosilicon derivatives only and by adding nanosilicas.

## Experimental

### Materials

All commercially available chemicals were used as received without any further purification. Poly(dimethyl-co-hydromethyl)siloxanes and vinyltrimethoxysilane were purchased from Gelest. Triethoxysilane and tetraethoxysilane were obtained from "Unisil" (Poland). Fumed silicas: Aerosil 130 (16 nm) and Aerosil300 (7 nm) were bought from Evonik. 3,3,3-Trifluoropropyltrimethoxysilane, 1H,1H,2H,2H-perfluorodecyltrimethoxysilane and other reagents, i.e. allyl glycidyl ether, Karstedt catalyst and solvents were supplied by Aldrich. All functionalized silicon compounds were obtained by hydrosilylation of a fluorinated olefin, namely 1,1,2,2,3,3,4,4-octafluoropentyl allyl ether, with triethoxysilane, poly(dimethyl-co-hydromethyl)siloxanes and octakis(hydrido, dimethylsiloxy)octasilsesquioxane. In the case of polysiloxane and silsesquioxane derivatives additional olefin was employed, namely vinyltrimethoxysilane or allyl glycidyl ether, in the process of consecutive hydrosilylation. Fluorofunctional silanes were synthesized according to the procedure described in Ref. 37 and polysiloxanes and silsesquioxanes containing mixed functional groups - according to the procedure presented in Refs. 38-40. The synthesis of

1,1,2,2,3,3,4,4-octafluoropentyl allyl ether was performed in the Williamson reaction using octafluoropentanol and allyl chloride<sup>41</sup>. Rhodium siloxide complex,  $[\{\text{Rh}(\text{OSiMe}_3)(\text{cod})\}_2]$  was synthesized according to the method described in the literature<sup>42</sup>. Glass plates were purchased from Thermo Scientific.

### Physico-chemical characterization

<sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75 MHz) and <sup>29</sup>Si MNR (59 MHz) spectra were recorded on a Varian XL 300 spectrometer at room temperature using CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> as solvents. FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases 16 scans at the resolution of 2 cm<sup>-1</sup> were collected for a spectrum. Measurements of contact angle were carried out using a Krüss GmbH instrument model DSA 100 Expert. The method of the measurement is based on the analysis of drop shape and it enables to perform measurements with the rate of up to 2000 f/s. The instrument was equipped with a fully automatic dosing system.

Acoustic AC Mode Atomic Force Microscopy (AAC-AFM) was applied to the surface characterization. The measurements were performed on a Scanning Probe Microscope Agilent 5500 equipped with silicon cantilevers BudgetSensors AllinOne working at the frequency of 150–400 kHz and dynamic mode with phase contrast imaging. Results of the measurements were analyzed using WSxM 5.0 Develop 6.5 software<sup>43</sup>. Sample roughness has been estimated on the basis of arithmetic mean roughness (Ra parameter) and root mean squared (Rq parameter).

### Modification of glass plates

**Cleaning procedure.** Glass plates immersed in a detergent solution were sonicated on an ultrasonic bath for 15 minutes, then rinsed with demineralized water, immersed in acetone and sonicated for additional 15 minutes followed by rinsing with demineralized water and drying in air at room temperature.

**Modification of glass plates with a solution of functionalized organosilicon compound by dip-coating method.** Functionalized silicon compounds (1-5) were applied directly on surfaces of glass plates. A 5% acidified ethanolic solution of an appropriate derivative was prepared for this purpose and the solution was applied directly on a cleansed substrate by the dip-coating method. The glass plate was immersed in such a solution for 5 minutes, taken out and dried in air for 3 minutes. Next it was immersed again in the modifier solution for 5 seconds followed by a 3-minute drying in air. The operation was repeated five times and then the plate was dried at 120°C for 1 hour.

**Modification of glass plates with a solution of functionalized organosilicon compound by sonication method** The procedure was basically the same as that described above, with the only difference that coatings were applied on glass plates by means of ultrasounds. The plates were placed in a beaker filled with a modifying compound solution and subjected to the action of ultrasounds.

**Modification of glass plates with a solution of functionalized organosilicon compound by chemical vapor method** Cleansed glass plates were placed in teflon stands followed by their transferring to the upper part of a steel autoclave. Then a modifying compound solution in toluene was poured onto the

bottom of the autoclave in such a way that the solution did not touch the glass plates. The autoclave was put into a heating chamber with a temperature of 120°C for 2 hours to enable organosilicon compound vapors to react with hydroxyl groups present on the surface of glass plates. After heating was over, the autoclave was opened, plates were taken out and dried at 120°C for 1 hour.

**Modification of glass plates with silica sol and then with functionalized organosilicon compounds** A mixture of 10 g tetraethoxysilane (TEOS), 40 g ethanol, 30 g water and 30 g aqueous ammonia was prepared, followed by vigorous stirring for 3 hours at room temperature. A suitable amount of such prepared sol (2.5 g) was mixed with 0.6 g of silica Aerosil 130 (particle size of 16 nm) or Aerosil 300 (particle size of 7 nm) and 47 g ethanol. The mixture was vigorously stirred for 30 minutes at room temperature and then glass plates were immersed in it for 15 minutes. To obtain an even layer on glass plates, sonication was applied. After the process was over, the plates were dried for 1 hour at 120°C. In the second step, glass plates were modified with a solution of functionalized organosilicon compound. The procedures were analogous to those used in the case of the modification with solutions of organosilicon compounds only. The operation was repeated five times and then the plates were dried at 200°C for 1 hour.

## Results and discussion

The glass surfaces were modified with fluorofunctional organosilicon compounds representing three basic types of derivatives, namely silanes, polysiloxanes and silsesquioxanes. Taking into consideration that hydrophobic properties are influenced to a significant extent by fluoroalkyl chain length, all the derivatives employed had the same substituent, namely octafluoropentyl group. Moreover, each of the compounds has a reactive group that, by the reaction with hydroxyl groups present on glass surface, forms a stable bond with a substrate. Our earlier research showed that, besides commonly used trialkylsilyl groups, also glycidyl groups are highly reactive. The former, via hydrolysis to silanols, undergo easy condensation with surface OH groups to form stable siloxane bonds, while in the case of the latter their oxirane ring undergoes rupture under the influence of hydroxyl groups, thus forming a bond to a substrate. All derivatives were obtained by hydrosilylation of allyl octafluoropentyl ether with triethoxysilane and hydrosilylation of vinyltrimethoxysilane or allyl glycidyl ether with poly(hydrimethyl-co-dimethyl)siloxane or octakis(hydrimethylsiloxy)octasilsesquioxane in definite stoichiometric ratios. Five derivatives, the formulas of which are presented in Fig. 1, were chosen for the study. Moreover, for the sake of comparison of hydrophobic properties, silanization of glass plates was performed with two commercially available fluorofunctional silanes, i.e. 3,3,3-trifluoropropyltrimethoxysilane (TFS), and 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (PFS).

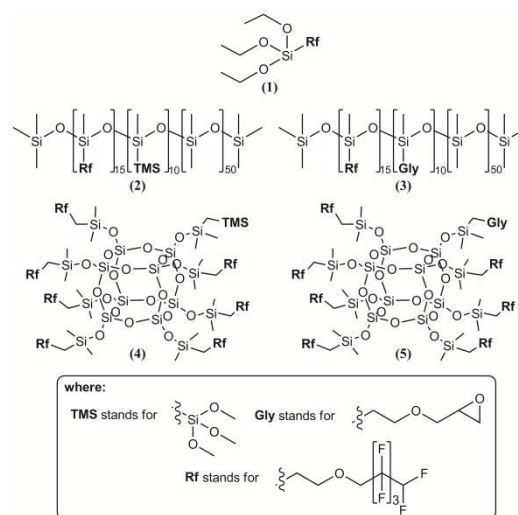


Figure 1. Fluorofunctional organosilicon compounds employed for the modification of glass plate surfaces.

At the first stage of the study, glass plate surfaces were subjected to modification with acidified 5% ethanolic solutions of the above compounds. After the modification, plates were subjected to drying at 120°C for 1 hour and then water contact angle (WCA) was measured. At first the modification was carried out using three methods: (i) by immersing a plate several times in a modifier solution, (ii) by immersing a plate in the analogous way, but under the action of ultrasounds, and (iii) by vapor phase deposition. However, the obtained results have shown that differences in water contact angles on surfaces modified with fluorofunctional polysiloxanes or silsesquioxanes by using the aforementioned methods were insignificant, which indicates that modification method has practically no effect on hydrophobic properties of surfaces. Only in the case of the modification with fluorofunctional silanes an increase in WCA was observed when the surface was modified by vapor phase deposition. The increase was caused by a greater volatility of this compound compared to polysiloxanes and silsesquioxanes which resulted in a higher concentration of this derivative in the vapor phase and this was reflected by a higher degree of surface coverage. However, to compare hydrophobic properties of different compounds it was necessary to create identical conditions of their application, which would be impossible in the case of poorly volatile polysiloxanes and silsesquioxanes. For this reason only the dip-coating under the action of ultrasound (ultrasound helped with a better and more uniform distribution of compounds on the surface) was used at the next stage of the study. WCA values for surfaces modified with all fluorofunctional silicon derivatives synthesized in this study as well as with two commercially available silanes (TFS and PFS), using the aforementioned method, are shown in Table 1.



Table 1. WCA values for glass plate surfaces modified with 5% solutions of different functionalized organosilicon derivatives by using dip-coating method under the action of ultrasound

| Compound | WCA [°]            |
|----------|--------------------|
| 1        | 97 <sup>(A)</sup>  |
| TFS      | 86                 |
| PFS      | 103                |
| 2        | 104                |
| 3        | 109 <sup>(B)</sup> |
| 4        | 117                |
| 5        | 119 <sup>(C)</sup> |

(A), (B), (C) - please refer to the Figure 4.

The obtained results show that modifications with all compounds employed in the study brought about the formation of hydrophobic surfaces. The lowest WCA values were found for the surfaces treated with fluorofunctional silanes. Furthermore, it is easy to see that WCA value is influenced by the length of fluoroalkyl chain (thereby by fluorine content in a compound). From among surfaces modified with different fluorofunctional silanes, the highest WCA values were observed for the surface modified with PFS, which has the longest fluoroalkyl chain. However, taking into consideration the fact that the above compound contains more than twice as much of fluorine atoms than silane (1), the difference in WCA values of the discussed surfaces (by 6°) is relatively small. The other commercial silane (TFS), that contains only three fluorine atoms, was characterized by the lowest WCA. However, it should be mentioned that in the latter case, the WCA value was influenced not only by the lowest fluorine content, but also by the length of chain, because the longer alkyl chain (including fluoroalkyl one) the greater hydrophobic properties. Taking into consideration that differences in WCA for the silanes appeared to be small, as well as the fact that the present study was aimed at determining the effect of silicon compound structure having the same fluoroalkyl substituents, the further part of this study was carried out with compounds 1-5 as the surface modifying agents. Analysis of results shown in Table 1 brings into conclusion that WCA is influenced not only by the number of fluoroalkyl groups in a molecule, but also by the structure of fluorine-containing compound. The highest WCA were found for surfaces modified by the use of silsesquioxanes (4 and 5). The comparison of the structure of different-type silicon compounds permits to assume that the modification with fluorofunctional silane (1) results in linking this compound to a point on glass plate surface, which in the case of favorable conditions is followed by condensation of a few silane molecules at the surface of the plate (see Fig. 2a). The molecules are linked to the surface in a rigid way. In the case of fluorofunctional polysiloxane, the surface becomes covered with a siloxane layer. Taking into account both flexibility of siloxane chain and statistical distribution of functional groups (Fig. 2b), one can expect that the chain is close to the surface only at the point of its linking, whereas its other part undergoes undulation and this will expose fluoroalkyl groups on the surface. Moreover, the polysiloxane layer will cover free hydroxyl groups on the surface, thus blocking them. In the case of silsesquioxane, their linking to the surface occurs only via one group, therefore silsesquioxane cage is flexible and due to this fact seven fluoroalkyl groups can be very well exposed on the surface (Fig. 2c).

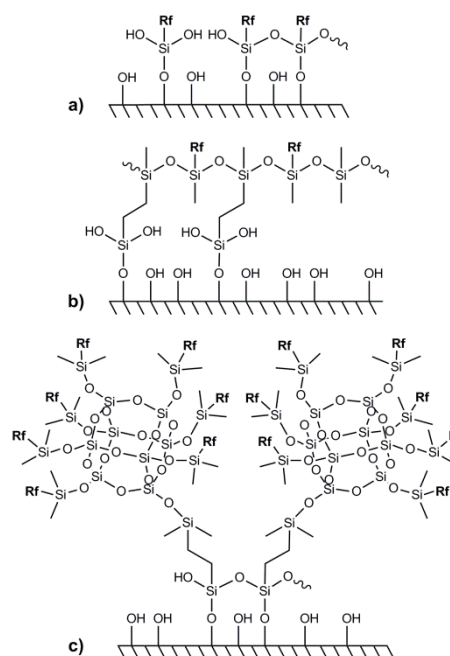


Figure 2. Exemplary way of linking between a glass substrate and a) fluorofunctional silane, b) trimethoxysilyl ethyl group-containing fluorofunctional polysiloxane, c) one trimethoxysilyl ethyl group-containing fluorofunctional silsesquioxane

Moreover, the analysis of WCA values for various polysiloxane and silsesquioxane derivatives shows that higher values were obtained for the derivatives containing glycidoxypopyl groups (Gly) compared to those containing trimethoxysilyl ethyl groups (TMS). The reason for the above fact can be the length of the chain that links a reactive group with the main siloxane chain or silsesquioxane cage. In the case of glycidyl derivatives, this chain is longer which results in a greater flexibility of the attachment to the surface, thus providing a better possibility for the orientation of fluoroalkyl groups. Thereby a greater surface diversification occurs which results in an increase in WCA. An example of epoxy group-containing polysiloxane linking to the surface is shown in Fig. 3.

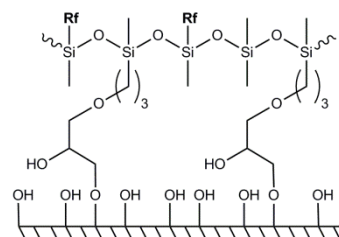


Figure 3. Exemplary way of linking between a glass substrate and epoxy group-containing fluorofunctional polysiloxane

Examples of drop shapes for selected systems (A-C) are presented in Fig. 4.

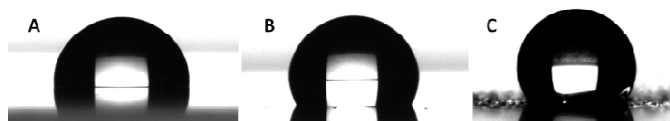


Figure 4. Examples of drop shapes for selected systems (A-C)

It is well known that maximum water contact angle on a perfectly smooth surface is  $120^\circ$ , and micro/nano structure must be developed for achieving superhydrophobic properties<sup>30</sup>. Synthetic superhydrophobic surfaces have been produced through various approaches, including the creation of a rough surface followed by coating with low surface energy substances. Many methods have been developed to obtain rough surfaces. From among these methods, colloid assembly is the most suitable one.

Employing the procedure described in the literature<sup>21</sup>, we have coated glass plates by using silica sol that was obtained by mixing aqueous ammonia with tetraethoxysilane (TEOS) in ethanol. After a two-hour stirring at  $60^\circ\text{C}$ , nanosilica (Aerosil 300) was added. To determine an optimal concentration of silica that was added to sol, we have prepared several solutions which were then contacted with glass plates. The latter were immersed in the sol for 5 minutes before the first dip-coating, and 5 seconds before the subsequent dip-coating. After each coating the substrate was dried at room temperature for 5 min, and this process was repeated 5 times. The modification was ultrasound-aided in order to obtain a better dispersion of silica in silica sol. The coated plates were then heated at  $200^\circ\text{C}$  for 1h. For the sake of comparison, another series was made in an analogous way with the additional use of ultrasounds. At the next stage, plates prepared in such a way were immersed in an acidified solution of a suitable fluorofunctional compound by using the dip-coating method. Contact angles on surfaces modified by fluorofunctional silane (1) and polysiloxane (2) derivatives are presented in Table 2.

Table 2. WCA values for surfaces treated with a mixture of silica Aerosil 300 and silica sol (at different concentrations) and then subjected to modification with fluorofunctional silane (1) or polysiloxane (2)

| Compound | WCA $^\circ$ on the surface modified with silica sol mixed with Aerosil 300 at concentrations given below |         |         |         |
|----------|---|---------|---------|---------|
|          | 5%:2%   | 5%:1.2% | 5%: .6% | 5%:0.3% |
| 1        | 91  | 106     | 95      | 95      |
| 2        | 111   | 125     | 121     | 110     |

Results presented in Table 2 show that the highest water contact angle was achieved for the surface pretreated with 5% solution of silica sol mixed with 1.2% Aerosil 300. This is why the above concentration was used in further studies. The mentioned WCA values are considerably higher than those observed for surfaces modified with solutions of fluorofunctional silicon compounds only. For this reason at the next stage of our study we have modified glass plates with silica sol according to the procedure described above using two kinds of nanosilicas: Aerosil 300 (particle size of 7 nm) and Aerosil 130 (particle size 16 nm). Such prepared glass substrates were treated with solutions of all types of fluorofunctional derivatives. All

modified surfaces were subject to WCA measurements results of which were presented in Table 3.

Table 3. WCA values for the surface pretreated with two types of Aerosil nanosilica dispersed in silica sol and then modified with fluorofunctional organosilicon derivatives using dip-coating method under the action of ultrasound

| Compound | Type of nanosilica | WCA $^\circ$       |
|----------|--------------------|--------------------|
| 1        | Aerosil 300        | 106                |
|          | Aerosil 130        | 117                |
| 2        | Aerosil 300        | 125                |
|          | Aerosil 130        | 134 <sup>(D)</sup> |
| 3        | Aerosil 300        | 135                |
|          | Aerosil 130        | 155 <sup>(E)</sup> |
| 4        | Aerosil 300        | 144                |
|          | Aerosil 130        | 160                |
| 5        | Aerosil 300        | 152                |
|          | Aerosil 130        | 167 <sup>(F)</sup> |

(D), (E), (F) - please refer to the Figure 5.

The obtained results explicitly show that Aerosil 130, i.e. the silica of greater particle size (16 nm), creates a greater surface roughness which results in a considerable increase in WCA after modification with organosilicon compound. Taking into consideration the kind of organosilicon compound employed for modification, one can notice that the tendency to the change in hydrophobic properties was maintained like in the case of modification of surfaces with solutions of organosilicon derivatives only, i.e. the lowest values were obtained for fluorofunctional silane (1) and the highest ones for silsesquioxane derivatives (4 and 5). Noteworthy is also the surface modified with polysiloxane (3) that was earlier covered with Aerosil 130. In this case a superhydrophobic surface was obtained, too. However, it is worth to add that the preparation of polysiloxane containing mixed functional groups as well as the price of the derivative are considerably more advantageous compared to silsesquioxane derivatives. Examples of drop shapes for selected systems (D-F) are presented in Fig. 5.

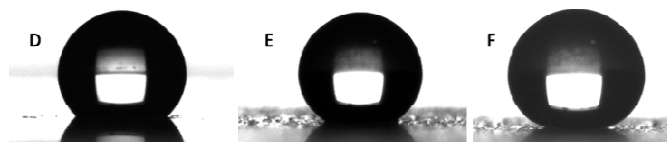


Figure 5. Examples of drop shapes for selected systems (D-F).

Our research has shown that surfaces subjected to the preliminary modification with silica of definite particle size, followed by a further modification with fluorofunctional silicon compound that can be stably bound to the substrate, become strongly hydrophobic. Bonding of silsesquioxanes, having cage structure, to preliminary modified glass surface results in its greatest diversification thereby in the best hydrophobic properties (the highest WCA values), particularly if they are linked via long group originating from glycidoxypopyl substituent (Gly). However, the application of polysiloxane (3), containing the same substituents, causes (due to the great flexibility of siloxane chain) an appropriate arrangement of siloxane on the rough surface and the best orientation of fluoroalkyl groups outside the layer. Just for this derivative and for functionalized silsesquioxanes one can observe the greatest increase in WCA (by 46, 43 and 48 degrees, respectively) caused by the diversification of surfaces by silica (Fig. 6).

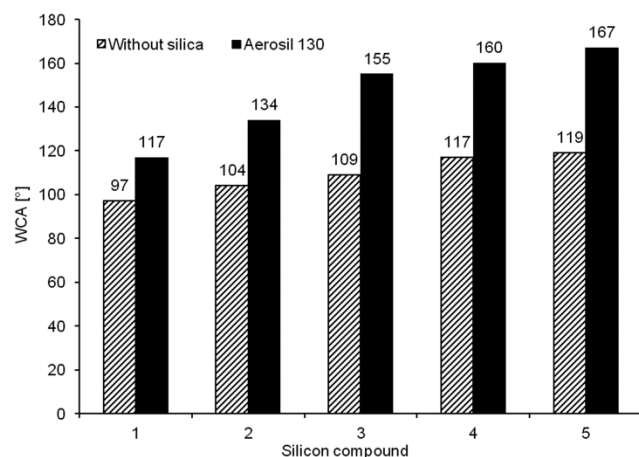


Figure 6. Change in WCA for surfaces modified with solutions of organosilicon compounds alone and additionally with the use of silica Aerosil 130, while using ultrasound-aided immersion method.

The morphology of surfaces of created coatings was studied also by atomic force microscopy and results of this study at its initial stage were quite surprising. Measurements of a non-treated plate and a silsesquioxane-covered plate showed that the non-treated plate has comparable (and sometimes even higher) roughness than the modified one. The measurements were repeated several times, using also new plates modified with the same compound, and results were almost the same as previously. To find how the roughness will be affected by silsesquioxanes having another number of functional groups, we have prepared two derivatives with different content of Rf:TMS groups, namely 6:2 and 4:4, respectively. The mentioned compounds were the subject of our earlier research<sup>44</sup>. A comparison of results obtained for non-treated plate and a series of plates covered by functionalized silsesquioxanes with different ratio of functional groups Rf:TMS showed that the non-treated plate was characterized by a slightly greater roughness than plates modified with the use of POSS containing 4 fluoroalkyl groups and 4 trimethoxysilyl groups and 6 fluoroalkyl and 2 trimethoxysilyl groups. The modification of the plate surface by the derivative containing seven fluoroalkyl and one trimethoxysilyl group brought about a small increase in the surface roughness. Root mean square deviation of surface Rq was found to be 0.35 nm for non-treated substrate and 0.23, 0.37 and 0.41 nm for substrates modified with the use of POSS whose ratios of functional groups Rf:TMS were 4:4, 6:2 and 7:1, respectively. Differences in the surface morphology were presented in Fig. 7.

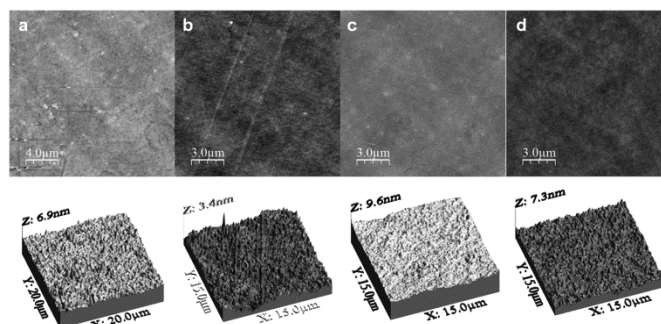


Figure 7. AFM images of a) non-treated glass plate, b) c) and d) glass plates modified with silsesquioxanes of Rf:TMS group ratios of 4:4, 6:2 and 7:1, respectively.

Results of the measurements of roughness (Rq) correlate well with results of water contact angle (WCA) carried out for the same substrates. We have established that WCA values increase with the rise in the number of fluoroalkyl groups present in a molecule of a modifier compound, as well as with increasing surface roughness. The effect of surface smoothing that was observed for substrates modified with the POSS derivative having the ratio of functional groups of 4:4 should be explained by the possibility of forming multidimensional structures on glass surface. The mentioned structures of a low degree of organization of fluoroalkyl chains are products of condensation of trimethoxysilyl groups (present in POSS) not only with the substrate but also between modifier molecules. This causes surface smoothing and reduces the number of accessible surface fluoroalkyl groups. The POSS derivative containing six fluoroalkyl and two trimethoxysilyl groups can still form extended surface structures, but their effect on the reduction in the surface roughness is somewhat smaller which, in combination with a greater content of fluoroalkyl groups, results in an increase in the surface hydrophobicity. In the case of the surface modified with functionalized organosilicon derivatives only, the highest wetting angle (117°) was found for the substrate treated with the derivative containing only one trimethoxysilyl and seven fluoroalkyl groups. This may be explained by the fact that the above derivative can be linked to the support via only one trimethoxysilyl group. This is why silsesquioxane molecules have a great freedom of orientation and a possibility of forming a homogeneous surface layer in which seven fluoroalkyl substituents can be well arranged on the surface causing its strong hydrophobization. Moreover, silsesquioxanes that are well-defined regular nanomolecules can level scratches occurring on a glass plate by partial filling them up. This is proved by the average distances between local maxima observed on surfaces of untreated glass plates. It results from the measurements performed for the roughness profile presented in Fig. 8 that the above maximum is 225 nm on the average.

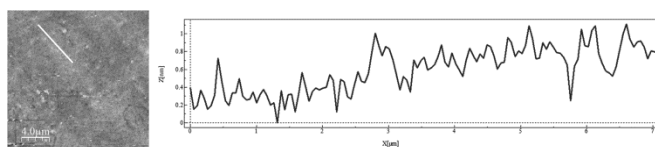


Figure 8. Line profile for untreated glass plate.



A totally different situation has been observed for surfaces modified with the use of functionalized polysiloxane (2) as shown in Fig. 9.

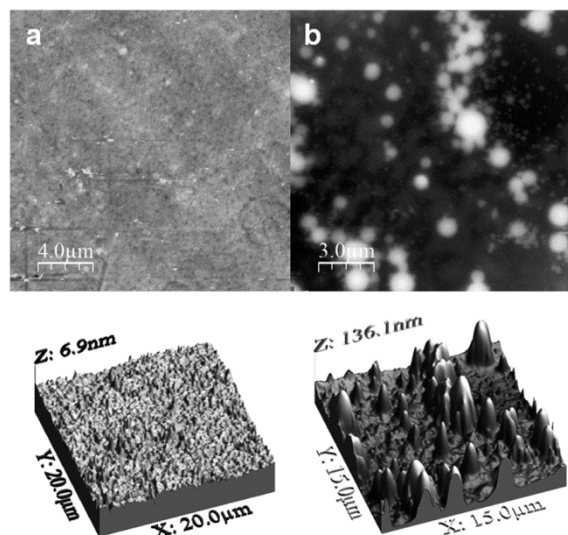


Figure 9. AFM images of a) untreated glass plate and b) glass plate treated with polysiloxane (2)

In this case a considerable rise in the surface roughness was observed ( $R_q$  is 26.8 nm). The surface coverage with polysiloxane results in the appearance of irregular oval structures. It can be explained by the great flexibility of siloxane chain and statistical distribution of functional groups in the chain. The orientation of the above groups on the surface results in the creation of a kind of domains. Long polysiloxane chain can, due to linking to several alkoxysilyl groups, undergo additional bending that results in over-exposition of fluoroalkyl groups. This is also a confirmation of the model presented in Fig. 2. This causes that we observe a greater surface roughness and, in spite of the fact that polysiloxane (2) does not contain so many fluoroalkyl substituents as silsesquioxane (4), water contact angle of the polysiloxane-modified surface is also high and equals to  $109^\circ$ .

Preliminary modification of glass plate surface certainly brings about an increase in its roughness and additional chemical modification with fluorofunctional organosilicon derivatives leads to the formation of superhydrophobic surfaces. Fig. 10 shows AFM images of the surface pretreated with silica sol and then modified with polysiloxane (2) and silsesquioxane (4).

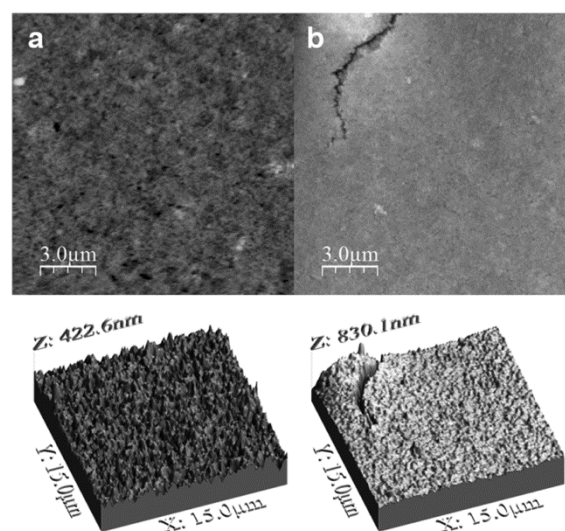


Figure 10. AFM images of glass plates modified with silica sol and then with a) polysiloxane (2), and b) silsesquioxane (4)

In both cases  $R_q$  is almost the same and equals to 58.2 nm. In the case of the plate covered with silica sol and then with silsesquioxane the layer is considerably thicker which results in some cracks, but generally the surfaces are homogeneous.

## Conclusions

Surfaces of glass plates were modified with five different organosilicon derivatives (silanes, polysiloxanes and silsesquioxanes) that contained the same fluoroalkyl substituents (octafluoropentylxypropyl, Rf) and groups enabling the formation of bonds to the substrate (trialkoxysilyl TMS or glycidoxypropyl Gly) and hydrophobic properties of the surfaces were compared. At first the modification was performed using three methods, however, due to their insignificant effect on hydrophobic properties, the further study was carried out with the use of ultrasound-aided dip-coating method. In each case hydrophobic surfaces were produced, however, the best effect (the highest values of wetting angle) was obtained for the modification with the use of silsesquioxanes (4 and 5). In comparison with other compounds studied, silsesquioxanes are characterized by relatively the greatest number of fluoroalkyl substituents (although the highest fluorine content occurs in the case of silane (1)) that are well exposed on the surface. The cage structure of silsesquioxane enables it to be linked to the substrate by one corner and the remaining seven corners with fluoroalkyl substituents contribute to the high hydrophobicity. Initially, it was supposed that the cage structure will lead to an increase in the surface roughness, however, AFM measurements have shown that cage dimensions are small enough to result in the effect opposite to the expected one, i.e. the modification with silsesquioxanes caused a reduction in the surface roughness. To increase the surface roughness two silicas, Aerosil 130 and Aerosil 300, were applied onto the plates from silica sol. Modification of such prepared surfaces with all silicon compounds mentioned above made it possible to create superhydrophobic surfaces in the case of compounds 3-5. The best effect was obtained for the modification with silsesquioxanes ( $WCA = 167^\circ$ ), however, polysiloxane also enabled to create a superhydrophobic surface ( $WCA = 155^\circ$ ).

The explanation of the above results should be sought in the great flexibility of siloxane chain that enables a good orientation of fluoroalkyl chains on the surface. Both in the case of polysiloxanes and silsesquioxanes it was found that the longer substituent that links them to substrate the higher surface hydrophobicity because the distance between the molecules and the surface is greater, which means that the surface roughness is also greater. Taking into consideration that the synthesis of fluorofunctional polysiloxane is simpler and cheaper than that of silsesquioxane, as well as the fact that the hydrophobizing activity of polysiloxanes is considerably more effective than that of most frequently applied fluorofunctional silanes, this group of derivatives seems to be the most promising from the point of view of practical application.

### Acknowledgements

We gratefully acknowledge the financial support from the Ministry of Science and Higher Education (Poland) for the project No. N N209 765640.

### Notes and references

<sup>a</sup> Adam Mickiewicz University, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland.

<sup>b</sup> Adam Mickiewicz University Foundation, Poznań Science and Technology Park, Rubież 46, 61-612 Poznań, Poland.

<sup>c</sup> Wielkopolska Centre of Advanced Technologies, Umultowska 89c, Poznań 61-614, Poland.

<sup>d</sup> Institute of Physics, Poznań University of Technology, Nieszawska 13a, Poznań 60-965, Poland

† Corresponding author: Hieronim Maciejewski, Adam Mickiewicz University Foundation, Poznań Science and Technology Park, Rubież 46, 61-612 Poznań, Poland, e-mail: maciejm@amu.edu.pl, tel.: +48 61 8279753, fax: +48 61 8279754

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- 1 Citations here in the format A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523; A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523.
- 1 X. Gao, L. Jiang, *Nature*, 2004, **432**, 36
- 2 V.A. Ganesh, H.K. Raut, A.S. Nair, S. Ramakrishna, *J. Mater. Chem.*, 2011, **21**, 16304
- 3 M. Farzaneh, D.K. Sarker, *J. Adhes. Sci. Technol.*, 2009, **23**, 1215
- 4 S.A. Kulinich, M. Farzaneh, *Langmuir*, 2009, **25**, 8854
- 5 T. Darmanin, F. Guittet, *J. Mater. Chem.*, 2009, **19**, 7130
- 6 J.A. Taylor, T.N. Krupenkin, T.M. Schneider, S. Yang, *Langmuir*, 2004, **20**, 3824
- 7 Y. Zhu, J. Zhang, J. Zheng, Z. Huang, L. Feny, L. Jiang, *Adv. Funct. Mater.*, 2006, **16**, 568
- 8 Z. Guo, W. Liu, B.L. Su, *J. Colloid. Interface Sci.*, 2011, **353**, 335
- 9 Y. Xiu, L. Zhu, D.W. Hess, C.D. Wong, *Nanolett.*, 2007, **7**, 3388
- 10 Q.F. Xu, J.N. Wang, I.H. Smith, K.D. Sanderson, *J. Mater. Chem.*, 2009, **19**, 655
- 11 L. Valtola, A. Koponen, M. Karesoja, S. Hietala, A. Laukkanen, H. Tenhu, P. Denifl, *Polymer*, 2009, **50**, 3103

- 12 N. Zhao, Q.D. Xie, L.H. Weng, S.Q. Wang, X.Y. Zhang, J. Xu, *Macromolecules*, 2005, **38**, 8996
- 13 G. Zhang, D.Y. Wang, Z.Z. Gu, H. Möhwald, *Langmuir*, 2005, **21**, 9143
- 14 L. Xu, J. He, *Langmuir*, 2012, **28**, 7512
- 15 L. Mammen, X. Deng, M. Untech, D. Vijayshanker, P. Papadopoulos, R. Berger, E. Riccardi, F. Leroy, D. Vollmer, *Langmuir*, 2012, **28**, 15005
- 16 X. Du, X. Li, J. He, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2365
- 17 X. Du, J. He, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1269
- 18 Y. Xiu, F. Xiao, D.W. Hess, C.P. Wong, *Thin Solid Films*, 2009, **517**, 1610
- 19 B.J. Basu, V. Hariprakash, S.T. Aruna, R.V. Lakshmi, J. Manasa, B.S. Shruthi, *J. Sol-Gel Sci. Technol.*, 2010, **56**, 278
- 20 H.M. Shang, Y. Wang, S.J. Limmer, T.P. Chou, K. Takahashi, G.Z. Cao, *Thin Solid Films*, 2005, **472**, 37
- 21 Q.F. Xu, J.N. Wang, K.D. Sanderson, A General Approach for Superhydrophobic Coating with Strong Adhesion Strength, *J. Mater. Chem.*, 2010, **20**, 5961
- 22 Y. Xiu, D.W. Hess, C.P. Wong, *J. Colloid Interface Sci.*, 2008, **326**, 465
- 23 A.V. Rao, S.S. Latthe, D.Y. Nadargi, H. Hirashima, V. Ganescan, *J. Colloid Interface Sci.*, 2009, **332**, 484
- 24 K.-Y. Yeh, K.-H. Cho, Li-J. Chen, *Langmuir*, 2009, **25**, 14187
- 25 M. Pagliaro, R. Ciriminna, *J. Mater. Chem.*, 2005, **15**, 4981
- 26 L.W. McKeen, Fluorinated Coatings and Finishes Handbook, *William Andrew Publ.*, New York, 2006
- 27 M.J. Owen, in, *Silicones and Silicone-Modified Materials* (S.J. Clarson, M.J. Owen, S.D. Smith, M.E. Van Dyke, eds.), *ACS Publ.*, New York, 2010, chap.9
- 28 Y. Hayashi, T. Yoneda, K. Matsamoto, *J. Ceram. Soc. Jpn.*, 1994, **102**, 206
- 29 N. Yoshino, *Chem. Lett.*, 1994, **4**, 735
- 30 B. Arkles, Y. Pan, Y.M. Kim, in, *Silanes and Other Coupling Agents* vol. 5 (K.L. Mittal ed) *VSP Utrecht*, 2009
- 31 C. Pasquet, C. Lonquet, S. Hamdami-Devarennes, B. Amedur, F. Ganachaud, in, *Silicone Surface Science* (M.J. Owen, P.R. Dvornic eds.) *Springer*, Dordrecht, 2012, chap. 5
- 32 F. Giuda-Pietrasanta, B. Boutevin, *Adv. Polym. Sci.*, 2005, **179**, 1
- 33 W. Choi, A. Tuteja, S. Chhatre, J.M. Mabry, R.E. Cohen, G.H. McKinley, *Adv. Mater.*, 2009, **21**, 2190
- 34 A. Tuteja, J.M. Mabry, in, *Silicone Surface Science* (M.J. Owen, P.R. Dvornic eds) *Springer*, Dordrecht, 2012, chap.6
- 35 C. Hartmann-Thompson Ed., *Application of Polyhedral Oligomeric Silsesquioxanes*, *Springer*, Dordrecht, 2011
- 36 B. Marciniak, H. Maciejewski, C. Pietraszuk, P. Pawluć, *Hydrosilylation A. Comprehensive Review on Recent Advances*, *Springer*, Dordrecht, 2009
- 37 H. Maciejewski, B. Marciniak, J. Karasiewicz, EP 2473514 (B1), 2012
- 38 H. Maciejewski, J. Karasiewicz, B. Marciniak, EP 2473551 (B1), 2013
- 39 H. Maciejewski, M. Dutkiewicz, B. Marciniak, EP 2473549 (B1), 2013
- 40 M. Dutkiewicz, H. Maciejewski, B. Marciniak, J. Karasiewicz, *Organometallics*, 30, (2011), 2149-2153

- 41 H. Maciejewski, J. Karasiewicz, B. Marciniec, *Polimery*, 2012, **57**, 449
- 42 B. Marciniec, P. Krzyżanowski, E. Walczuk-Guściora, W. Duczmal, *J. Mol. Catal.*, 1999, **144**, 263
- 43 I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705
- 44 H. Maciejewski, J. Karasiewicz, M. Dutkiewicz, B. Marciniec, *Silicon* (submitted for publication), 2014