I Introduction

Even though the discovery of sol–gels was made more than 150 years ago by Ebelmen,1 elaboration of sol–gel coatings still is the subject of intense developments, especially after the first report by Geffcken and Berger in the 1930s demonstrating the possibility to obtain oxide coatings from alkoxides on industrial glasses.2,3 Thanks to its processing under mild conditions, the sol–gel technology is therefore one of the most privileged routes to produce hybrid functional thin films. A variety of metal alkoxides (Si, Zr, Ti, etc.) used as precursors and a large range of organic compounds that can be mixed with lead to an infinite combination of materials with new properties.4,5 Besides, colloidal dispersions can be easily processed in various shapes such as powders, fibers, coatings or bulk monolithic products, with an accurate control of their structure and chemical composition. Therefore, sol–gel thin films have attracted a good deal of attention from industry for the implementation of low-temperature functional coatings.6

Numerous research studies were undertaken toward the introduction of specific organic or polymeric compounds into sol–gel networks in order to achieve the desired properties. Because of their dual structure, organosilanes were found to be highly relevant compounds. Indeed, alkoxysilane moiety is able to covalently bind inorganic matrices such as glass or metals by hydrolysis–condensation while the organic part can provide additional properties or react with organic matrices.7 Among them, fluoroalkylsilanes (FASs) have been widely employed in the coating industry because of their outstanding hydro- and lipophobic properties due to their low surface energy.8 The scientific community agrees that a surface is hydrophobic if the static water contact angle is higher than 90°.9 It was demonstrated that decreasing the surface energy of FASs could lead to a maximum contact angle of 115° with regularly aligned closest hexagonal-packed-CF3 groups.10

Distribution of fluoroalkylsilanes in hydrophobic hybrid sol–gel coatings obtained by co-condensation†

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Whether it is for imparting anti-corrosion, anti-fogging or stable optical properties, hydrophobic coatings have been at the center of numerous research studies these last few decades. While surface perfluorination and surface roughening have been thoroughly studied, few studies discuss the introduction of fluoroalkylsilanes (FASs) directly into sol–gel networks in order to obtain water-repellent silica films. The latter method, referred to as co-condensation, is yet easier to perform (one-pot and mild conditions) and in accordance with industrial standards. However, so far its implementation to achieve maximum surface hydrophobicity has not been well-controlled and the influence of such FAS molecules trapped in the sol–gel network on the mechanical properties has not been investigated. In this work, how the co-condensation method affects the distribution of the fluorinated additives in the sol–gel network is studied by obtaining a precise XPS profile of the FASs within the material. The water-repellent, optical and mechanical properties of such coatings were evaluated. From these results, the one-step co-condensation method was proved to exhibit similar properties to a classic multi-step surface silanization. Moreover, by getting a better understanding of the mechanisms involved during the film formation, it is henceforth possible to accurately control the concentration of FASs needed to optimize the water-repellency. Besides, it was demonstrated that these results were not impacted by the chemical structure of the FASs, thus highlighting various alternative synthesis strategies of interest. Based on these conclusions, the co-condensation is, for the first time, demonstrated to be a method of choice to prepare water-repellent sol–gel coatings, presenting the significant advantage compared to classic silanization to allow an accurate adjustment of the FAS concentration in order to achieve maximum hydrophobicity.

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Two approaches can be employed to lower the surface energy of sol–gel hybrid films. The first method corresponds to a surface treatment of the inorganic layer, which is performed for self-assembled monolayers on a silicon wafer.\textsuperscript{19} It requires three steps: (i) the preparation of a pure inorganic layer, (ii) the activation of the reactive hydroxyls at the surface and (iii) silanization with hydrophobic alkoxysilane derivatives. Numerous techniques for such surface treatment have been reported over the years in the literature using chemical or physical techniques.\textsuperscript{20} It was demonstrated that entire coverage of the surface was achieved according to this procedure, leading to maximum hydrophobicity. In the second strategy, the FASs are introduced into the sol–gel formulation as co-precursors. Even though this method is much less employed than the silanization, it is particularly compliant with industrial standards. Indeed, it requires only one step which corresponds to the deposition of the fluorinated sol–gel formulation, without any preliminary activation of the surface involving a combination of bases and strong acids or UV–ozone cleaning.\textsuperscript{21} Via this technique, Urata \textit{et al.} obtained with a solution of FAS and tetramethoxysilane final dynamic wetting properties comparable or superior to those of the best perfluorinated textured and flat surfaces developed so far.\textsuperscript{22} This method will be referred to in this paper as co-condensation. However, because competition can eventually take place between trapping of FASs in the network or their migration toward the surface during the coating process, complete coverage of the surface with these fluorinated additives is therefore less straightforward here. Indeed, unlike the silanization method, two populations of FASs can coexist inside the material, one located at the surface and one trapped inside the bulk, which could modify the final properties of the sol–gel layer. In order to compare these two methods, the organization of these additives in the sol–gel network obtained by co-condensation and the resulting surface and bulk properties for both materials have been investigated.

Moreover, alternative synthetic pathways to produce FASs have been implemented in this study, showing significant advantages compared to conventional routes. However, these different reactions lead to chemical modifications of the FAS structure which might modify the properties of the resulting sol–gel films. As a matter of fact, urethane and ether bonds have been introduced between the fluorinated and alkoxysilane moieties instead of the traditional alkyl bond.\textsuperscript{23} In order to determine the prospects of these molecules as “easy-to-prepare” hydrophobic additives, the influence of their chemical structure has been evaluated on several properties such as surface hydrophobicity and mechanical and thermal resistance properties. Similar results to those of the commercial molecule were obtained with these particular FASs which implies that they could replace it in most applications.

II Experimental section

II.1 Materials

Ethanol (EtOH), methanol (MeOH), diethyl ether (Et₂O), tetrabutyl ammonium hydroxide (TBAH), sodium hydroxide (NaOH), allyl bromide, hydrochloric acid (1 M HCl), sulfuric acid (H₂SO₄), anhydrous sodium sulfate, 1H,1H,2H,2H-perfluoro-1-octanol, triethoxysilane, 3-(triethoxysilyl)propyl isocyanate, tetraethyldisiloxanilic (TEOS), a platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt catalyst), and Pluronic® F127 (EO₁₀₆PO₇EO₁₀₆) were purchased from Sigma-Aldrich and used as received. Dynasylan F8261 (FAS-R) was provided by Evonik and used without any further purification. The ¹H NMR spectrum of FAS-R is provided in ESI S1 (Fig. S1).\textsuperscript{†} Perfluoro-1-octanol was obtained from Altochem and distilled prior to use.

II.2 Synthesis of tridecafluoroctyl [3-(triethoxysilyl)propyl] carbamate (FAS-U)

\begin{align*}
1H,1H,2H,2H-\text{Perfluoro-1-octanol} \quad (3.68 \text{ g, } 10.1 \text{ mmol}) & \quad \text{and} \quad 3-(\text{triethoxysilyl})\text{propyl isocyanate} \quad (2.5 \text{ g, } 10.1 \text{ mmol}) \\
\text{were introduced in a one-neck round bottom flask under nitrogen. The mixture was stirred at } 90 \text{ °C for } 24 \text{ h. The target product (6.18 g, yield: 100%) was obtained without any purification step.} \\
\text{1H NMR (CDCl₃, 300 MHz): } & \delta \text{ (ppm) } 0.63 (m, 2H), 1.22 (t, 9H), 1.63 (m, 2H), 2.45 (m, 2H), 3.17 (m, 2H), 3.81 (q, 6H), 4.35 (t, 2H), 5.05 (b, 1H) \text{ (ESI S1, Fig. S2).}\textsuperscript{©}
\end{align*}

II.3 Synthesis of tridecafluorooctyalkyl ether\textsuperscript{26}

\begin{align*}
1H,1H,2H,2H-\text{Perfluoro-1-octanol} \quad (5 \text{ g, } 13.7 \text{ mmol}), \text{diethyl ether} \quad (2.42 \text{ g, } 32.7 \text{ mmol}), \text{tetrabutyl ammonium hydroxide} \quad (0.09 \text{ g, } 0.27 \text{ mmol}) \quad \text{and} \quad \text{allyl bromide} \quad (4.98 \text{ g, } 41.2 \text{ mmol}) \quad \text{were taken in a two-neck round-bottom flask equipped with a condenser. The mixture was stirred, and } 20 \text{ M NaOH} \quad (2.42 \text{ g, } 30.21 \text{ mmol}) \quad \text{was added carefully.} \\
\text{The mixture was then placed at } 50 \text{ °C for 6 hours under magnetic stirring. When the reaction was proved to be complete by } \text{1H NMR analysis, diethyl ether was added to the mixture and the product was washed five times with water.} \\
\text{The organic phase was dried with anhydrous sodium sulfate and filtered. The target product (4.7 g, yield: 85%) was obtained after removal of the solvents under reduced pressure at } 30 \text{ °C.} \\
\text{1H NMR (CDCl₃, 300 MHz): } & \delta \text{ (ppm) } 2.42 (m, 2H), 3.72 (t, 2H), 4.00 (dt, 2H), 5.26 (m, 2H), 5.90 (m, 1H).
\end{align*}

II.4 Synthesis of tridecafluorooctyl[3-(triethoxysilyl)propyl] ether (FAS-E)\textsuperscript{27}

Tridecafluoroalkyl ether (4.6 g, 11.4 mmol) and triethoxysilane (2.24 g, 13.7 mmol) were taken in a two-neck round bottom flask. The mixture was stirred at 90 °C, and the Karstedt catalyst (100 ppm per allyl function) was added with a calibrated micropipette under nitrogen. The reaction was carried out until complete disappearance of the allylic groups, easily detected by \textsuperscript{1H NMR spectroscopy. The platinum catalyst was treated with activated charcoal added into the reaction medium, previously diluted in toluene. The mixture was stirred for 3 hours and was then filtered. After removal of the solvent under reduced pressure at 50 °C, the product was distilled at 115 °C in order to eliminate the tridecafluoroethyl-terminated propenyl-ether, formed during the hydrosilylation. The target product (3.85 g, 60%) was then obtained.} \textsuperscript{4} \text{H NMR (CDCl₃, 300 MHz): } \delta \text{ (ppm) } 0.65 (m, 2H), 1.22 (t, 9H), 1.70 (m, 2H), 2.39 (m, 2H), 3.43 (t, 2H), 3.70 (t, 2H), 3.81 (q, 6H) \text{ (ESI S1, Fig. S3).} \textsuperscript{†}
II.5 Film processing

Co-condensed thin films (Co-SG) were prepared from solutions composed of TEOS/FAS/Pluronic® F127/HCl (1 M)/H2O/EtOH with a respective molar ratio of 1 – a/a/0.0001/0.15/5/40 (0.001 < a < 0.01). The co-condensed films prepared with FAS-R, FAS-U and FAS-E are, respectively, denoted in the rest of the study as follows: Co-SGR, Co-SGU and Co-SGE. EtOH, H2O, and HCl were first added to a glass vial followed by TEOS, FASs and F127. The presence of F127 in a low proportion ensures good wettability of the solution with the substrate during coating processing. Solutions were stirred and then placed at 70 °C for 30 minutes before use. Xerogel films were prepared by dip-coating (ACEdip equipment from SolGelWay) (100) silicon wafers in the previous solutions at room temperature and at a relative humidity of 5% up to the disappearance of the drying line. The withdrawal speed was adjusted between 2 and 3 mm s⁻¹ to fix the final thickness at around 80 ± 10 nm. The as-prepared films were then aged at 200 °C for 5 minutes. Samples prepared for XPS analysis were deposited with higher withdrawal speeds to attain thicknesses between 110 and 120 nm.

Silanized films (SAM-SG) were prepared by dip-coating silicon wafers in a solution composed of TEOS/F127/HCl/H2O/EtOH, according to the same protocol. To achieve optimal silanization, any contaminants must be removed from the sol–gel thin films and the reactive hydroxyls must be activated. Therefore, the following cleaning procedure was selected since its effectiveness has been demonstrated by Cras et al.¹ The sol–gel thin films were first treated with a solution of MeOH : HCl (1 : 1) for 30 minutes, rinsed in H2O and dried under a stream of N2 prior to the subsequent cleaning step to avoid any contaminations. The samples were then incubated in a concentrated solution of H2SO4 for 30 minutes, exhaustively rinsed in H2O and dried under N2. The surface modification was carried out by immersing the sample for 1 h in a 2 wt% solution of FAS-R in toluene; then the samples were heavily rinsed with fresh toluene to remove weakly bound fluoroalkylsilanes and were dried under N2. The samples were then aged at 120 °C for 5 min and then at 200 °C for 5 min.

II.6 Chemical characterization

¹H NMR spectra were obtained using a Bruker Avance 300 (300 MHz) spectrometer equipped with a QNP probe at room temperature. Chemical shifts were, respectively, referenced to the peak of the residual non-deuterated solvent CDCl₃ at 7.26 ppm.

II.7 Contact angle (CA)

Hydrophobicity was evaluated by static contact angle measurements performed with a device using a simplified experimental setup.²⁸ A deionized water drop (2 μL) was deposited on the surface, and the contact angle was measured after processing the picture using ImageJ software. For each thin film, 5 measurements were performed on different areas of the coating and the average value was given as the surface contact angle. The same procedure with hexadecane was performed to assess the oleophobicity of the films.

II.8 Ellipsometry

Spectroscopic ellipsometry and environmental ellipsometric porosimetry (EEP) measurements were performed on a UV-visible (from 210 to 1000 nm) variable-angle spectroscopic ellipsometer (Woollam M2000V) equipped with a controlled atmosphere cell in which relative humidity was controlled by mass flow controllers. The EEP setup and the data analysis protocol were previously described.²⁹ The data were analysed with WVase32 software using a one-layer Cauchy model. The measured reflectivity spectra were described by a two-layer stack model consisting of a Si substrate covered by a SiO₂ layer and a hybrid silica thin film as a top layer. From the characteristics of the oxidized substrate, the thickness of the sol–gel layer was then obtained from the best match between the calculated and experimental spectra. Thicknesses of Co-SGR, Co-SGU, Co-SGE (co-condensed films including, respectively, FAS-R, FAS-U and FAS-E) and SAM-SG were between 75 and 90 nm while the refractive index varied from 1.41 to 1.43.

II.9 Crockmeter

Mechanical properties were estimated in terms of resistance to abrasion using the crockmeter test that consists in rubbing of the top of the films with a pad. The latter pad was covered with a calibrated fabric (ISO test method 105-F09). It was loaded with a constant 5 N charge and was moved back and forth in a straight line. A single cycle corresponded to a back and forth motion of the pad.

II.10 Solvent extraction

The chemical resistance of the FASs was assessed by determining the ability of the FASs to remain covalently linked to the sol–gel network after prolonged contact with chemicals. The substrates coated with the functional thin films were first immersed for 5 minutes in chloroform and then sonicated for 10 minutes.²⁹ The substrates were then removed from the solution, dried at 80 °C under vacuum, and characterized by gravimetric analysis and static contact angle measurements. The solvent fractions were dried, and the solid residues were analysed by ¹H NMR.

II.11 Physical characterization

II.11.1 AFM. Structural investigation of the surface of the hybrid sol–gel films was performed by atomic force microscopy, using a PSIA XE-100 AFM setup. The obtained spectrum is presented in ESI S2.†

II.11.2 TGA. Thermogravimetric analyses were performed on a TGA550 High-Resolution from TA Instruments. The samples were heated in an alumina crucible from room temperature to 700 °C under a nitrogen flow. The experiments were carried out at a heating rate of 10 °C min⁻¹. All analyses are available in ESI S3.†

II.11.3 X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a UHV system with a base pressure in the range of 10⁻¹0 mbar, using a monochromated Al-Kα excitation source
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\[ (h\nu = 1486.6 \text{ eV}) \]. The binding energy scale of the spectrometer was calibrated by setting Au 4f\textsubscript{7/2} at 84 eV with respect to the Fermi level. Photoelectrons were collected with an Omicron EA 125 energy analyzer at a 30 eV pass energy, and the spectra were analyzed using CasaXPS software. A Shirley-type background subtraction was performed on the spectra followed by a fit by means of a non-linear least-squares deconvolution program, using Gaussian–Lorentzian peak shapes. The fluorine/silicon (F/Si) ratio was evaluated from curves fitted to the F 1s and Si 2s spectra. The areas were corrected for the relative sensitivity factor (RSF) and transmission (T), and the F/Si ratio was calculated according to the following equation:

\[
\frac{F}{Si} = \frac{A(F)}{A(Si)} \times \frac{RSF(Si)}{RSF(F)} \times \frac{T(Si)}{T(F)}
\]

Depth profiles were obtained by combining XPS analyses and etch cycles. An ion gun was used to etch the sample with Ar ions (800 eV, 4 μA).

III Results and discussion

III.1 Synthesis of the FAS molecules

Fluoroalkylsilanes, exhibiting perfluorinated alkyl chains longer than six carbons, have been subject to recent regulations as it was highlighted that their oxidative degradation leads to the generation of perfluorooctanoic acid (PFOA). Indeed, this molecule was found to be persistent in the environment, toxic and prone to bio-accumulate in bio-organisms.\textsuperscript{22,23} The limitation of the perfluorinated chain length leads to a decrease of the water- and oil-repellency performances of the functionalized films since these properties are in part related to the number of fluorine atoms in the molecule’s backbone.\textsuperscript{23} However, it was demonstrated by Urata et al. that surface wettability was independent of the \( R_i \) chain length \( \{C_{(X-1)2}F_{X}, \ 3 \leq X \leq 17\} \) for co-condensed hybrid films. It was thus decided to focus the study here on perfluorinated chains bearing 6 carbons which comply with environmental standards. Moreover, a recent study carried out by Ballarin et al. demonstrated that the lack of hydrophobicity due to a lower fluorine content could be balanced by introducing an amide spacer between the fluorinated and silane moieties, thanks to the formation of intermolecular hydrogen bonds.\textsuperscript{23} This observation is of great importance since it highlights the fact that FAS performances are not only dependent on fluorinated moieties but are also related to the nature of the entire chemical structure. For this reason, three different chemical spacers were studied here to investigate their effects on the functional sol–gel film properties. Hydrophobicity, solvent resistance, and mechanical and thermal properties were evaluated for each material including the different FASs. FAS-R \((C_{15}-F_{13}C_{2}H_{4}Si(OCH_{2}CH_{3})_{3})\) was commercially available whereas FAS-U \((C_{6}F_{13}C_{2}H_{4}OC(O)NHCH_{2}Si(OCH_{2}CH_{3})_{3})\) and FAS-E \((C_{6}F_{13}C_{2}H_{4}OC(O)H_{2}Si(OCH_{2}CH_{3})_{3})\) were specially designed to incorporate particular linkers in between the fluorinated and alkoxysilane moieties (Fig. 1). A urethane embedded spacer was selected since, like the amide functionality, hydrogen bonds can be formed between the oxygen and nitrogen atoms.\textsuperscript{24,25} These intermolecular interactions are known to favor the orientational molecule stability, and therefore, enhanced mechanical properties are expected.\textsuperscript{26} Besides, it was also demonstrated that the presence of hydrogen bonds limits the release of molecules.\textsuperscript{27} Regarding the compound FAS-E, an ether bond was introduced to give more flexibility to the molecule, thanks to the higher freedom of rotation of the C–O–C bond compared to the C–C bond.\textsuperscript{28} Better abrasion resistance was also expected due to the presence of heteroatoms in the molecule’s backbone.\textsuperscript{29} Besides, another point investigated here was to see if the longer alkyl spacer of FAS-E might have an impact on the water-repellency, despite the presence of the oxygen atom in the backbone.\textsuperscript{30,31}

Two specific synthetic pathways were then implemented to introduce either a urethane or an ether functionality between the fluorinated and alkoxysilane moieties of the FASs. The same fluorinated precursor \(1H,1H,2H,2H\)-perfluoro-1-octanol, commercially available, was used for both syntheses. The embedding of the urethane group was accomplished by the reaction between the fluorinated alcohol and an isocyanato-alkyl terminated silane (Fig. 1a). This synthesis presents numerous substantial advantages which makes it particularly suitable for industrial development. Indeed, it is a solvent-free, moderate-temperature process which does not require any catalyst for activation. Moreover, the reaction is selective and does not need any purification steps, leading to excellent yields.

FAS-E is synthesized by a two-step reaction: (i) the functionalization of the fluorinated alcohol with an allyl-ether via the Williamson reaction and (ii) the hydrosilylation of the allyl-ether with triethoxysilane leading to the desired molecule (Fig. 1b). During the addition of the silane to the carbon double bond, isomerization occurs, leading to 20 mol% of FAS-terminated propenyl-ethers. These side-products are, however, easily eliminated by distillation.\textsuperscript{32} Despite the reduced selectivity, this synthetic pathway presents significant advantages compared to the procedure employed for the preparation of the commercial compound. FAS-R is prepared from fluorinated compound-functionalized vinyls, such as \(1H,1H,2H\)-perfluoro-1-octene, which are not reactive toward alkoxysilanes in the presence of the platinum catalyst. Therefore, the synthesis requires at first hydrosilylation with trichlorosilane, followed by an alcoholysis step with alkoxide salts in order to avoid the formation of hydrochloric acid during the process (Fig. 1c). The use of trichlorosilane leads to high selectivity (above 90%) but necessitates a closed system at high pressure with some specific apparatus, because of its low boiling point and its corrosive character.\textsuperscript{33} It was demonstrated that these two reaction stages can be avoided if the hydrosilylation is carried out with a rhodium-based catalyst.\textsuperscript{34} However, the selectivity decreases below 80%, and the catalyst price is a serious issue.

III.2 Determination of the FAS critical concentration for a complete coverage of the sol–gel surface

Only a few examples of sol–gel solutions containing FASs as co-precursors have been described in the literature. The scarce use of the co-condensation method can be explained by the fact that there is no accurate control of surface functionalization which
is a key point to attain high surface hydrophobicity. Indeed, Sermon et al. showed that, with this method, lower surface hydrophobicity was obtained compared to a classic FAS adsorption.35 Besides, Urata et al. observed lower fluorine concentrations at the surface when FAS were co-condensed with tetramethoxysilane than when the FAS were fully-packed by grafting.14 By getting a deeper understanding of how FASs get organized in the sol–gel network, the co-condensation method could be mastered more efficiently in order to achieve optimal water-repellency and compete with the silanization procedure.

To determine the distribution of FASs within the sol–gel layer, the formulation containing FAS-R as the co-precursor (Co-SGR) was studied as a representative model. It was demonstrated that for such materials only the contribution of the FASs’ low surface energy influenced the hydrophobic behavior since the surface was proved to be smooth by AFM measurements (ESI S2†). To obtain a hydrophobicity similar to the one obtained by the classic silanization, there has to be therefore sufficient FASs in the formulation to bind every reactive site on the film surface. This particular concentration of FASs is defined as the critical concentration \( n_c \), corresponding to the molar ratio between the FAS and TEOS molecules initially present in the formulation. For their subsequent determination, it was assumed that all the FAS molecules migrate to the surface before the complete condensation of the network. Because the critical concentration will also depend on the surface before the complete condensation of the network. This particular concentration of FASs was estimated to be 3.4 \( \times 10^{14} \) molecules per \( \text{cm}^2 \). Therefore, in our case, the density of FASs was estimated to be 3.4 \( \times 10^{14} \) molecules per \( \text{cm}^2 \), which corresponds to the density obtained by Van de Grampel and others for F6-thiol molecules whose structure is similar to the one studied here.38,39

Since the amount of FASs in the solution is very low compared to the proportion of SiO\(_2\) (i.e. \(<2\) mol%), it was estimated that the density of the material was equivalent to the density of a pure silica xerogel material (\( \sim 1.8\) g cm\(^{-3}\)). Therefore, the number of moles of silica can be formulated according to eqn (I), with \( t \) being the thickness of the sol–gel layer (nm) and \( S \) the surface area (cm\(^2\)):

\[
n_{\text{SiO}_2} = \frac{\rho V}{M_{\text{SiO}_2}} = \frac{1.8 \times S \times t \times 10^{-7}}{60} \tag{I}
\]

For a surface of 1 cm\(^2\), the number of FAS molecules required to have a maximum coverage is 3.4 \( \times 10^{14} \), i.e. 0.56 \( \times 10^{-5} \) mol. From eqn (I), the eqn (II) can be deduced relating the critical concentration and the thickness:

\[
n_c = \frac{n_{\text{FAS}}}{n_{\text{SiO}_2}} = \frac{0.19}{t} \tag{II}
\]

Contact angle measurements and XPS analysis were then carried out in order to confirm the veracity of the several assumptions stated above, which are (i) the complete migration of FASs before condensation and (ii) the saturation of the surface with 3.4 \( \times 10^{14} \) molecules per cm\(^2\). To do so, contact angles of multiple materials prepared with different \( n_c \) (\( n_{\text{FAS}} \), in the formulation and \( t \) is the thickness in nm) ratios were measured in order to evaluate the enrichment of FASs at the surface. The first set of experiments was performed by fixing \( \alpha \) and varying the thickness. However, the range of \( \alpha \) attainable was limited by the difficulty to obtain high thicknesses for this

![Fig. 1 Synthetic pathways of FAS-U (a), FAS-E (b) and FAS-R (c).](image)
formulation. Thicknesses from 30 to 110 nm were obtained for withdrawal speeds between 0.2 and 5 mm s\(^{-1}\). Therefore, another set of measurements was performed by fixing the thickness and varying \(\alpha\) enabling us to obtain a wider range of \(\alpha t\). The results are presented in Fig. 2. Similar profiles were obtained for these two sets of experiments which confirms the good correlation between the \(\alpha t\) ratio and the surface hydrophobicity.

Two trends with very different slopes can be seen in Fig. 2. For \(\alpha t\) between 0 and 0.15, the contact angle increases from 36\(^\circ\) to 94\(^\circ\). Even for very low amounts of fluorinated additives, a significant increase of the contact angle is observed. Indeed, by adding to the formulation only 0.1 mol% of FASs (\(\alpha = 0.001\)), the contact angle increases from 36\(^\circ\) to 81\(^\circ\). These results confirm the progressive enrichment of the surface with FASs with increasing \(\alpha\). Given the high hydrophobicity measured for these concentrations, it can be supposed that most of the FASs are located at the surface. For \(\alpha t\) higher than 0.15, the contact angles still increase but to a much lesser extent (from 94\(^\circ\) to 104\(^\circ\)) which suggests that the surface is reaching saturation. The fact that the intersection between these two trends occurs at an \(\alpha t\) value close to the estimation of \(a_c t\) (=0.19) is consistent with our definition of the critical concentration. Nevertheless, above the determined critical concentration, the contact angles continue to increase and the maximum coverage is supposed to be attained. A possible explanation is that further layers of FASs continue to increase and the maximum coverage is supposed to be attained. A possible explanation is that further layers of FASs are bound to the superior layer during the dip-coating process leading to superior contact angles. The contact angles were thus measured on a coating at \(\alpha t = 0.8\), before and after rinsing the surface with ethanol and drying it under argon. A loss of 3\(\times\)10\(^4\) leading to superior contact angles.

III.3 XPS study of the distribution of FASs in the sol–gel network

However, this study is not sufficient to assess with certainty that \(a_c t\) is equal to 0.19 since no relationship between the density of fluorinated molecules at the surface and the contact angle has been established yet. Therefore, in order to determine more accurately the organization of FASs in the sol–gel network and evaluate the surface saturation, X-ray photoelectron spectroscopy (XPS) was performed.

XPS is a useful method to probe the surface composition of polymers and inorganic materials over a few tens of molecular layers. The spectra were obtained at a take-off angle of 20\(^\circ\), corresponding to a probing depth of 4.2 nm (\(\Delta h\)).\(^{48}\) To obtain a depth profile of the sol–gel material, sputtering with Ar ions was carried out to abrade the material. Calibration of the abrasion depth as a function of ion bombardment time was previously performed on a silica xerogel by measuring the thickness of the coating by ellipsometry before and after abra- tion. XPS analysis was carried out at first on a sample (A) with a FAS concentration close to the critical concentration (\(\alpha = 0.0016\) and \(t = 112\) nm, giving \(\alpha t = 0.18\)) and exhibiting a contact angle of 99\(^\circ\). The second sample (B) was prepared from a formulation containing \(\alpha = 0.005\) FAS and deposited with a thickness of 121 nm (\(\alpha t = 0.61\)). Therefore, the concentration of 3.2 was higher than \(a_c t\) and the contact angle was equal to 103\(^\circ\). The general spectrum obtained for both samples confirmed the presence of silicon, oxygen, fluorine and carbon atoms.

While Si 2s, Si 2p, O 1s and F 1s peaks were fitted with single components,\(^{46}\) the C 1s region was best fitted with 5 contributing bands (Fig. 3a). Details of the peaks’ attribution are presented in ESI S4.\(^{†}\) Regions I and II, at BE = 280.7 eV and BE = 282.1 eV, were assigned to CH\(_2\) and CH\(_3\), respectively, belonging to the ethoxysilane moieties and the CH\(_2\)–CH\(_3\) of the fluoralkylsilsilane. At BE = 285.0 eV, region III was ascribed to CF\(_2\)–CH\(_2\), and at BE = 287.3 eV, region IV was ascribed to CF\(_3\)–CF\(_2\) and CF\(_2\)–CF\(_3\). Region V, at BE = 289.9 eV, corresponds to the moiety CF\(_3\). The CF\(_3\) and CF\(_2\) were clearly resolved from the other components because of their high electronegativity.\(^{47}\) By doing so, the proportions of each region were consistent with the percentage of the ascribed carbons in the FAS molecules.

The calculated and measured fractions of FASs (molecules and atoms) are reported in Table 1. For sample A prepared at a concentration close to the critical concentration, the F/Si atom

![Fig. 2](image-url)  
**Fig. 2** Contact angle measurements as a function of the parameter \(\alpha t\). The dashed line corresponds to the theoretical established critical concentration (\(a_c t = 0.19\)).

![Fig. 3](image-url)  
**Fig. 3** (a) XPS C 1s region (bold line) fitted with five components (normal lines). (b) XPS F 1s region before (red line) and after 3.5 nm Ar etching (green line) for \(\alpha = a_c\).
ratio measured at the surface is equal to 0.33, which corresponds to \( \alpha_s = 0.025 \) (13 atoms of fluorine per FAS). This value is 16 times higher than the expected F/Si = 0.021 value if all FASs (\( \alpha = 0.0016 \)) were homogeneously distributed in the sol-gel network, suggesting that most FASs are located at the surface at the end of the process. This is confirmed by the XPS analysis of the F content upon etching, as reported in Fig. 3b. Indeed, at 3.5 nm below the surface, the proportion of FASs is almost negligible, and after 35 nm abrasion, no more FASs can be detected in the material. A shifting of the XPS F 1s region after abrasion toward low binding energies can be observed in Fig. 3b attesting to the change of environment for the fluorine atoms located inside the bulk of the sol-gel layer. These observations suggest that the migration of FASs toward the surface is quasi complete before the network consolidation. The difference in surface energies between the surface and the liquid bulk is likely responsible for this phenomenon since it creates a thermodynamic driving force leading to the preferential segregation of the fluorinated additives toward the air interface to reduce the system’s interfacial tension.

Regarding the sample B that was prepared from a formulation containing \( \alpha = 0.005 \) FAS and with a thickness of 121 nm (see Table 1), the amount of FASs is about three times higher than what would be needed to reach the critical concentration \( (\alpha = 0.61 \text{ vs. } \alpha_s = 0.19) \). XPS investigations show that the F/Si ratio at the surface is equal to 0.4 (\( \alpha_s = 0.031 \)) which is 24% higher than \( \alpha_s \) measured on sample A. This result is consistent with the fact that the previous sample had a FAS concentration close to the critical concentration, and thus, the surface may not be entirely covered with fluorinated molecules. XPS analysis was also performed after several abrasions on sample B, enabling us to draw the F/Si ratio distribution profile within the material (see Fig. 4). Fig. 4 shows that the F/Si ratio decreases dramatically from 0.4 to reach a minimum at 0.04 after 2 nm etching. Interestingly, the F/Si ratio starts to increase with further etching to reach 0.1 at 20 nm, after which it starts to slowly decrease. Here again, if the FAS molecules are homogeneously distributed in the silica network, a theoretical F/Si ratio of 0.005 \( \times \) 13 = 0.065 must be found all over the coating depth profile. The dashed line, corresponding to this theoretical F/Si ratio, is shown as a reference for comparison and to better illustrate the transversal mass transport involved during formation. The black bars represent the concentration of fluorine present in each 4 nm transversal slab deduced experimentally by XPS after each etching step. The sum of these bars corresponds to 41% of the total amount of fluorine in the films, given by the dashed line. The remaining 59% of fluorine is distributed in the slabs of 4 nm film thickness represented by the grey bars. The distribution is made by extrapolation to fit as much as possible the global tendency given by the experimental black values. The obtained histogram reveals the presence of two maxima (at the surface and around 20 nm from it) and two minima (at a few nm from the surface and in the half bottom part of the film). The minima and maxima present on the top part of the film are correlated and correspond to the formation of a depletion layer created by the diffusion of the FASs towards the surface as already mentioned. The presence of such a depletion layer has been deduced from crosslinked polymer networks containing fluorinated polymeric dangling chains, studied by simulation by Esteves et al.

However, in this particular case, the depletion was attributed to a reorientation of the fluorinated dangling chains toward the air interface with a thickness of this zone corresponding to the chain’s length. In our sol-gel coating, the depletion layer is much larger than the FAS molecule length, which is about 1 nm, suggesting that not only molecular reorientation but also mass transfer is necessarily involved. Indeed, during evaporation, FAS molecules diffusing and reaching the surface are promoted by the surfactant effect described for sample A. Since in the case of sample A (\( \alpha = 0.18 \)) most FASs are found at the surface, we can state that the mass transfer is very efficient and proceeds fast enough to be completed before total evaporation and stiffening of the network. The same statement can thus be made for the more concentrated sample B (\( \alpha = 0.61 \)) for which more FASs are present to saturate the surface. However, once the surface saturation is achieved, the remaining FASs should be homogeneously distributed inside the film which according to the experimental results in Fig. 4 (inset) is not the case.

### Table 1: Calculated and measured fractions of FAS molecules and fluorine atoms in the films’ bulk and at the film surface for both A and B samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \alpha = \text{FAS/Si formulation} )</th>
<th>( t ) [nm] thickness</th>
<th>( \alpha_t )</th>
<th>( F_{\text{atom}}/\text{Si film calculated} )</th>
<th>( F_{\text{atom}}/\text{Si surface} )</th>
<th>( \alpha_s = \text{FAS/Si surface} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0016</td>
<td>112</td>
<td>0.18</td>
<td>0.021</td>
<td>0.33</td>
<td>0.025</td>
</tr>
<tr>
<td>B</td>
<td>0.005</td>
<td>121</td>
<td>0.6</td>
<td>0.065</td>
<td>0.4</td>
<td>0.031</td>
</tr>
</tbody>
</table>

Fig. 4 F/Si ratio distribution profile in the bulk material for \( \alpha = 3.2 \alpha_s \), with an inset highlighting the repartition of FASs with respect to the theoretical F/Si ratio in a homogeneous network.
Moreover, the clear first depletion zone corresponding to \(-3.4\%\) of the total fluorine content does not compensate for the enrichment of the surface that corresponds to \(+16.6\%\). Even more puzzling is that an enrichment of \(+9.9\%\) at the film center and the depletion in the bottom part of the film should not be expected as no evident driving force exists for such mass transport. As a result, the experimental fluorine distribution profile cannot be explained with a simple diffusion governed by agglomeration at the surface of the FASs. Additional hydrodynamic phenomena, likely related to instabilities due to Marangoni’s stresses created during thin film evaporation, must be considered to fully understand this complex mechanism (Fig. 5). Indeed, convective flows occurred during the formation of the film due to an evaporation-driven surface tension gradient in the liquid layer leading to the enrichment of FASs from a low to a high surface tension area.\(^{44,45}\) Moreover, in addition to these convective effects, the evaporation taking place at the film–air interface creates a gradient of viscosity that progressively increases during this step, making the understanding of the depletion even more complex. Further in situ time-resolved investigations of this phenomenon under different processing conditions would be required to better understand it, but this is out of the scope of the present article.

III.4 Sol–gel coating properties

It was demonstrated that for a concentration above \(\alpha_c\), the FASs are non-homogeneously distributed in the entire material. Therefore, they differ from materials prepared by traditional grafting (SAM-SG), due to the presence of FASs at the surface and inside the bulk. Moreover, being introduced as co-precur-sors, their orientation at the surface might be different from the one obtained with a self-assembled monolayer. These distinctions can lead to different surface and bulk properties for the resulting thin films. So far, neither the mechanical resistance nor the solvent resistance of these fluorinated co-condensed films was studied whereas they are expected to be subjected to such external stresses.\(^{14}\) Besides, these properties have not been compared to the ones of SAM-SG materials obtained by classic silanization. Therefore, this study was extended to the comparison of Co-SG materials including various FASs with SAM-SG coatings. Surface sol–gel properties were analyzed by contact angle measurements, and thermal and mechanical resistance tests. The internal hydrophobicity of the bulk material was assessed by ellipsometric porosimetry which is an accurate tool to assess the refractive index and the thickness as a function of the relative humidity and the percentage of porosity. The concentration of the fluorinated additives \((\alpha_f)\) in the Co-SG materials was fixed at 4.2 \(\alpha_f\) in order to observe their influence at the surface and in the bulk. It is important to state here that, when \(\alpha_f > 16 \alpha_c\), the formulation does not wet correctly the surface of the substrate, even at high temperature, preventing the formation of a homogeneous coating.\(^{46}\) Such high FAS concentrations are thus disregarded.

III.4.1 Thermal durability of the fluorinated hybrid thin films

Thermal curing had an important effect on the final film structure since it governs the material’s stability, porosity, and surface area and the nature of the chemical interface, to cite a few.\(^{47}\) However, the presence of organic fluorinated additives greatly limits the range of curing temperatures due to their thermal decomposition. Therefore, the optimal conditions for the curing treatment of the materials have to be predetermined in order to find the best compromise between keeping the FASs’ integrity and consolidating at the most the sol–gel network. To do so, each FAS-based material was treated for 5 minutes at the following temperatures: 120 °C, 150 °C, 200 °C, 250 °C, 300 °C and 350 °C. The contact angles were measured afterward to follow the thermal degradation of the FASs. Fig. 6a shows that, up to 200 °C, the water-repellency is maintained for Co-SG and SAM-SG materials with contact angles between 100 and 110°, which implies that the degradation of the FASs did not occur yet. After a treatment at 250 °C, the contact angle measured for Co-SGU drops by 7°, attesting to the beginning of the degradation of the FAS-U molecules. For Co-SGU and Co-SGE materials, the contact angles are, respectively, equal to 49° and 43° after a treatment at 300 °C. These values are close to the contact angle of a silica layer,\(^{48}\) which means that almost all the fluorinated parts of the FASs located at the surface have been thermally removed. The lower thermal resistances of FAS-U and FAS-E can be explained by the presence of heteroatoms in the urethane and ether spacers which are more easily cleavable than carbon–carbon bonds. Concerning Co-SGR, the thermal resistance is similar to the one of SAM-SG, and both coatings still remain water-repellent after a thermal curing at 350 °C for 5 min.

From these results, it can be deduced that curing at 200 °C is suitable for preparing FAS-based sol–gel materials since no loss
of water-repellency has been observed at this temperature. Sol-gels can also be consolidated at moderate temperatures but for a more prolonged period of time. Different time periods of curing at 200 °C, from 10 min to 240 min, were then tested to determine the best conditions to prepare such materials. In Fig. 6b, it can be seen that no decrease of contact angles happens after a curing time of 90 min for both Co-X and SAM-X materials. The hydrophobicity starts to decline for Co-SGR after 120 min at 200 °C. However, both materials are still hydrophobic after 240 min at 200 °C (θ = 97° and 103°, respectively, for Co-SGR and SAM-SG).

From these results, it was demonstrated that the chemical spacer has an influence on the water-repellency of the sol-gel material, since urethane and ether functionalities are more easily cleaved than alkyl spacers at high temperatures. However, for a thermal treatment limited to 200 °C, the performances are similar between the three FASs. Besides, it has been demonstrated that the preparation methods (silanization or co-condensation) did not influence the thermal properties of the hybrid sol-gel coatings. As a result, a thermal treatment at 200 °C for 5 minutes was selected for the rest of the study since it was proved to be sufficient to obtain a consolidated network while avoiding any degradation of the FASs. Further investigations were carried out to evaluate the thermal stability of the different FASs using thermogravimetric analysis (TGA) and in situ thermal ellipsometry. The results, presented in ESI S3,† revealed first that the thickness and refractive index of the layers constantly decrease with increasing temperature as a result of the network cross-linking and the associated elimination of volatile H2O and EtOH. TGA, performed on the pure FAS, shows temperatures of decomposition lower than what is observed for the films, suggesting that FASs bonded to a sol-gel silica network are more resistant to thermal degradation.

III.4.2 Water- and oil-repellency of the fluorinated hybrid thin films. Since the FASs are intended to be used as hydrophobic and oleophobic additives, surface wettability is one of the key factors to study. Static CA values with water and hexadecane are reported in Fig. 7 for the different fluorinated hybrid thin films treated for 5 min at 200 °C.

Both materials exhibit contact angles with water above 100° which demonstrates the highly hydrophobic character of these sol-gel layers. The contact angle value obtained for SAM-SG is in accordance with the ones reported in the literature for self-assembled monolayers of a perfluorinated alkyl chain length of 6 carbons.12 It can be seen in Fig. 7 that the contact angles obtained with the different Co-SG layers are in the same range as those for the SAM-SG. This result shows that the chemical structure of the spacer does not influence the surface energy of the sol-gel layer for this length of the perfluoroalkyl tail.21 The contact angles were also measured in the case of drops of hexadecane in order to evaluate the oleophobic character of these sol-gel layers. SAM-SG exhibits higher oil-repellency (θ = 72°) than the Co-SG layers whose contact angles are between 58 and 64°. This difference can be explained by a different orientation of the fluorinated chain at the surface, in the case of co-condensation.

Since contact angle analysis only gives information on surface wettability, further investigations were made by environmental ellipsometric porosimetry (EEP). This analysis consists in measuring the variations of the refractive index in optical layers during adsorption/desorption of selected vapors inside the pores of the film. From these results, the pore geometry, pore size, surface area, porous volume and mechanical properties of micro- and mesoporous layers can be determined.24 Here, adsorption-desorption isotherms of Co-SG and SAM-SG are obtained to (i) characterize more thoroughly the materials developed in this study and (ii) determine the influence of FASs inside the bulk on water adsorption. Both samples, Co-SGR and SAM-SG, were exposed to increasing and decreasing relative vapor pressure (0 < P/P0 < 1). The refractive index was found to vary from 1.41 to 1.43 and 1.43 to 1.44, respectively, for Co-SGR and SAM-SG, when exposed to 0 to 100% relative humidity (Fig. 8).

As can be seen in Fig. 8a, the adsorbed volume of water increases progressively until reaching 5 and 4 vol%, respectively, for Co-SG and SAM-SG. The desorption curve follows the same trend without hysteresis. The pore size distribution could not be deduced from the Kelvin model since no capillary condensation occurs. The pore dimensions can thus be estimated to be in the range of micropores (<2 nm, Fig. 8b) which is in accordance with the type 1 isotherms observed with these coatings. Since both materials exhibit similar adsorption-desorption isotherms and pore distributions, it can be deduced that the preparation method has no influence on the characteristics of the films. Besides, it also demonstrates that the presence of FASs inside the bulk of Co-SG does not limit the water vapor penetration. This result is consistent with the fact that the FAS concentration in the bulk is too low to impart hydrophobicity.

III.4.3 Mechanical and chemical durability of the fluorinated hybrid thin films. Another important requirement for functional coatings is the retention of their properties upon external constraints. One particularly good example is the damage caused by windshield wipers to hydrophobic coatings dedicated to improve vision in heavy rain.29 Multiple studies have been carried out to improve the life-time of hydrophobic coatings upon abrasion. Two main strategies based on inherent conditions for water-repellency were developed these last few
years. The first method consists in developing specific nanostructures that are able to maintain their surface roughness after abrasion.\textsuperscript{36–38} The second approach, dedicated to the conservation of a low surface energy material, particularly contributed to the development of self-replenishing polymeric surfaces. This technology consists in recovering the surface properties upon damage thanks to the self-segregation of fluorinated groups covalently linked to the polymer network toward the air interface. However, for sol-gel networks, this last method cannot be applied. Indeed, the concentration of FASs in the bulk was proved not to be sufficient to impart hydrophobicity. It would require an overly high concentration of FASs in the formulation which would prevent a homogeneous deposition by dip-coating. This result is, in fact, in contradiction with previous statements on co-condensed hydrophobic sol-gel layers.

Even though self-replenishing properties could not be achieved according to this method, it was important to determine the influence of the presence of FAS in the bulk material on the mechanical properties of the film since phase segregation might occur between the silica and the fluorinated additive which might alter the material cohesion.\textsuperscript{43} The influence of the chemical nature of the spacers on the FASs’ abrasion resistance was also investigated (Fig. 9). The mechanical properties were evaluated by measuring the decrease of contact angle, indicating the progressive loss of FASs, over domestic abrasion using a crockmeter device (as described in the Experimental section).

The thicknesses of the coatings after 100, 250, 500, 750 and 1000 cycles were measured by ellipsometry (data not shown). The thicknesses remained unchanged after 1000 cycles which proved the good mechanical resistance of these hybrid sol-gel films and thus, the non-detrimental effect of having FASs present inside the sol-gel layer. Therefore, only the resistance to abrasion of the FASs located at the surface is investigated here. As can be seen in Fig. 9a, for both FAS-based films, the contact angles stay relatively constant upon mechanical abrasion with values above 90°. The variations of water contact angles after 1000 cycles for Co-SGR, Co-SGU, Co-SGE and SAM-SG are, respectively, 6°, 1.5°, 7.2° and 1.2°. Lower losses of contact angles are obtained for SAM-SG and Co-SGU. The grafting method appears to produce coatings less sensitive to abrasion than the co-condensation method. However, the urethane spacer seems to compensate for the lower abrasion resistance of co-condensed functional thin films since the decrease of contact angle is very close to the one obtained for SAM-SG. The presence of hydrogen bonds might increase the cohesion between the FASs located at the surface, limiting their degradation upon abrasion. Moreover, oil contact angle measurements were performed before and after 1000 abrasion cycles. No significant loss of oleophobicity was observed for Co-SGU and Co-SGE whereas a decrease of 8° of the oil contact angle was obtained for Co-SGR. This result can be explained by the orientation of the FAS-R molecules which is more susceptible to be modified by mechanical abrasion since no consolidation is induced by hydrogen bonds and the chains are not flexible enough to absorb the abrasion impacts.

In addition to mechanical constraints such as scratches or rubbing, sol-gel films can also come into contact with cleaning solvents, which can alter the surface properties of the coatings. Therefore, in order to evaluate the chemical resistance of the FASs, the different Co-SG materials were subjected to a prolonged immersion in solvents, as described in the Experimental section. After immersion and sonication of the FAS-based thin films in chloroform, a gravimetric analysis of the coatings was performed. No loss of weight was observed, and the contact angles remained the same after the test. Besides, the $^1$H NMR analysis of the solvent did not show any trace of FASs. These results attest that neither FASs nor silica was removed even after harsh extraction and thus, demonstrate the high chemical resistance of these three Co-SG layers.

IV Conclusions

A detailed study of the co-condensation method with fluoroalkylsilanes for the elaboration of water-repellent sol-gel coatings has been presented. As maximal hydrophobicity is obtained when the film surface is saturated with FASs, the concept of a critical concentration ($\alpha_c$) was put forward for the first time in this particular system. An equation relating this concentration to the sol-gel coating thickness was thus established enabling us to prepare hydrophobic sol-gel materials knowing the exact proportion of FASs to introduce to achieve maximum water-repellency.
A distribution profile of the FASs localized in the entire material was also obtained by accomplishing successive abrasions followed by XPS analysis. It was demonstrated that the FAS dispersion in the profile is a complex phenomenon that could be partly explained by mass transfer and hydrodynamic considerations. From these results, the tendency of FASs to migrate toward the air interface until their complete saturation before the complete condensation of the network was confirmed and the existence of a depletion zone beneath the surface was in particular highlighted for the FAS concentration above $\alpha_c$.

In order to investigate the influence of this particular preparation method, the surface and bulk properties of the FAS-based thin films were also compared to the ones of a self-assembled monolayer on a sol–gel film. It was demonstrated that fluorinated sol–gel layers obtained by co-condensation show similar results in terms of hydrophobicity, and mechanical and chemical resistance up to a thermal treatment of 350 °C. Some efforts were also made on the synthesis of two FAS molecules (FAS-U and FAS-E) which presents significant advantages compared to the industrial method. These two compounds exhibit similar results to the commercial molecule as those obtained by grafting, this method is for the first time proved to be an efficient way to prepare water-repellent coatings. Moreover, its ease of use (one step and no cleaning treatment) and the possibility to accurately control the surface saturation in FAS make this method particularly appealing for industrial development. Besides, the co-condensation can also be applied to the elaboration of super-hydrophobic coatings and thus can satisfy the increasing need for self-cleaning materials. Therefore, we hope that this study may serve as an incentive for the development of such techniques.

Conflicts of interest

There are no conflicts to declare.

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Notes and references