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Perfluoropolyether-based organic–inorganic hybrid coatings

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Abstract

Perfluoropolyether-based organic–inorganic hybrids were prepared by sol–gel process and applied as functional coatings onto glass substrates. Contact angle analysis and X-ray photoemission spectroscopy were carried out in order to characterize the surface of the prepared coatings. A strong hydrophobic and lipophobic character was observed for all tested compositions. The wettability behaviour was found to be dependent on both the coating technique and the reaction time of the sol–gel reaction. A strong surface segregation of perfluoropolyether segments was noted for all the prepared samples as evidenced by XPS analysis. On the basis of the obtained results, these materials could be used as functional coatings to prepare water and oil repellent glasses or other substrates.

Keywords: Organic–inorganic hybrids; Perfluoropolyether; Hydrophobic and oleophobic coatings

1. Introduction

Organic–inorganic hybrids (also named ceramers) are increasingly important materials due to their extraordinary properties deriving from the synergism between the properties of each individual component. Among the several ways to obtain this class of materials, probably the most prominent ones are the incorporation on a nanometric scale of inorganic moieties in organic polymers through the in situ formation of an inorganic network, the incorporation of preformed dense inorganic structures (clusters or particles), the formation of hybrids using porous or layered inorganic materials either by interpenetration of the organic polymers into the voids, or by exfoliation of the inorganic material [1].

These materials have gained much interest due to the remarkable change in properties such as mechanical, thermal, electrical and magnetic compared to pure organic polymers. Several applications have been already developed for this kind of hybrids materials [2] in particular in the field of protective coatings of both organic and inorganic substrates.

Thanks to its mild operative conditions, the most commonly employed preparation procedures for these materials are based on the sol–gel process [3] which lead to the formation of the inorganic network by starting from liquid precursors such as metal alkoxides (typically tetraethoxysilane) and organic oligomers preferably with suitable reactive groups. In fact, the covalent bonding between organic and inorganic components can lead to the formation of a crosslinked structure in which the organic and inorganic moieties are phase separated on a micro- or nano-scale, but the resulting material is macroscopically uniform.

The final morphology of these hybrid materials, and thus also their physical–mechanical properties, is strictly dependent on the characteristics of the organic polymer such as its molecular weight and its solubility in the sol–gel solution and the presence and the number of reactive functionalities.

In this study, the organic component was based on a commercial perfluoropolyether (PFPE) [4,5] which presents the typical properties of fluorinated-products [6]. In particular, PFPEs are characterized by very low glass transition temperatures (about −120 °C), chemical inertia, solvent and high temperature resistance, barrier properties, low coefficient of friction, hydrophobicity and lipophobicity and in particular very low surface energy. In fact,

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depending on the molecular weight, surface tension of linear PFPE varies in the range 14–25 mN m^{-1}, at least 10–15 mN m^{-1} lower than other conventional polymers, with few exceptions such as polyethylene, polypropylene and polysiloxane [7]. Furthermore, PFPEs are extremely non-polar substances and their very low solubility parameters (typically in the range 11–12 (J ml^{-1})$^{1/2}$) [4] lead to a marked thermodynamic incompatibility with most of the common organic polymers and solvents, other than with water and aqueous solutions. For this reason, pure PFPE cannot be directly used in the sol–gel process because of the impossibility to find a common solvent for the fluorinated oligomer and the other reactants (tetraethoxysilane and water). In order to overcome this drawback we modified the PFPE oligomer by preparing block copolymers containing polycaprolactone segments at both ends, leading to an organic material soluble in solvents commonly used in sol–gel processes. In previous papers [8,9] we demonstrated that the fluorinated segments of poly(caprolactone-*b*-perfluoropolyether-*b*-caprolactone) (PCL–PFPE–PCL) triblock copolymers tend to migrate to the outer surface due to the strong thermodynamic driving force to minimize the surface energy. The same behaviour was also noted in the case of polymer blends [10,11] and thus a similar mechanism of surface segregation can be in principle expected in the case of hybrid systems containing PFPE segments.

These organic–inorganic hybrid materials can be potentially used as functional coatings to prepare water and oil repellent glasses or, in general terms, to modify the surface characteristics of several substrates. At the best of our knowledge, the use of PFPE for the preparation of ceramers by using the sol–gel process was reported only by Wojcik and Klein [12] who prepared transparent, crack-free and water repellent organic–inorganic hybrids based on PFPE diol diacrylate and on perfluoroalkylsilane. Only few other examples are reported for the preparation of hydrophobic and lipophobic materials obtained by sol–gel approach [13–16].

In a previous study [17] we reported the preparation and the surface characterization (in terms of water contact angle measurements) of ceramers prepared with PCL–PFPE–PCL block copolymers and tetraethoxysilane having an organic phase content ranging from 20 to 80 wt%. The wettability of the final materials was found almost independent on the bulk ratio between organic and inorganic components indicating that in all cases the surface segregation of the fluorinated PFPE segments was high enough to give a very high hydrophobic character to the coating surface.

In the present work we investigated the surface properties of the same kind of PFPE-based organic–inorganic hybrids having a lower organic content (from 5 to 20 wt%) in order to verify the possibility to use small amount of PFPE leading to less expensive inorganic-rich systems able to confer the desired surface properties (hydrophobicity and lipophobicity). In addition, the effect of the method of application of the coating (manual dip-coating or spin-coating) has been investigated.

2. Experimental

2.1. Materials

α,ω-Triethoxysilane terminated poly(caprolactone-*b*-perfluoropolyether-*b*-caprolactone) block copolymers were prepared starting from a commercial product supplied by Solvay Solexis named Fluorolink® E (previously named Fomblin® Z-DOL TX) having a molecular weight of 2200 g mol^{-1}. Details about the synthesis procedure and the molecular characterization of the copolymers were reported in literature [17]. The materials were coded as TXCL(*x*)Si in which *x* represents the number-average degree of polymerization of the polycaprolactone segments of the copolymer.

The molecular structure of the copolymer can be represented by the following formula:

$$\begin{aligned}&\mathrm{(EtO)_3Si{-}(CH_2)_3{-}NH{-}CO{-}[O(CH_2)_5{-}CO]_x}\\&\mathrm{{-}(OCH_2CH_2)_nOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2O}\\&\mathrm{(CH_2CH_2O)_n[CO{-}(CH_2)_5O]_x{-}CO{-}NH{-}(CH_2)_3{-}Si(OEt)_3}\\&\text{(simplified structure : }\mathrm{(EtO)_3Si{-}PCL{-}PFPE{-}PCL{-}Si(OEt)_3})\end{aligned}$$

where the constituent units –CF_2CF_2O– and –CF_2O– are randomly distributed along the macromolecular chains with a p/q ratio of 0.9 and an average value of n of 1.5.

Tetraethoxysilane (TEOS, purchased from Aldrich), tetrahydrofuran (THF, Carlo Erba) ethanol (EtOH, Carlo Erba) and hydrochloric acid at 37% concentration (Carlo Erba) were used as received without further purification.

2.2. Preparation of organic–inorganic hybrids

TXCL(*x*)Si/TEOS mixtures were dissolved in THF at a concentration of about 20 wt/vol%, then EtOH (to make the system miscible), water (to promote the hydrolysis reaction) and HCl (as catalyst) were added at the following molar ratios (with respect to ethoxide groups of both TXCL(*x*)Si and TEOS):EtO-EtOH:H_2O:HCl = 1:1:1:0.05.

A typical preparation was as follows: 2.0 g of a TXCL(*x*)Si/TEOS mixture were added to 8 ml of THF in a screw-thread glass vial and mixed until a homogeneous solution was obtained. Then EtOH, water and HCl (37 wt% solution) were added under vigorous stirring at room temperature for about 10 min. The closed vial was placed in air circulating oven at the temperature of 70 °C for different times (t_r = 1 or 3 h) in order to allow the partial progress of the sol–gel reaction. Then the sol–gel solution was deposited onto microscope glasses previously cleaned by washing in standard RCA1 solution (NH_4OH:H_2O:$_2H_2O$ = 1:1:5) and rinsed in bi-distillated water, both by manual dip-coating or by spin-coating obtaining a typical coating thickness of 1–3 and 0.3–0.4 μm, respectively. After a period of 30 min at room temperature, samples were subjected to a thermal post-treatment at 100 °C for 2 h.

The final hybrids were coded as TXCL(*x*)Si/SiO_2 *y*:*z*, in which *y*:*z* represents the nominal weight ratio of organic and inorganic components assuming the completion of the sol–gel reactions reported below:

$$\begin{aligned}&Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 + 4EtOH\\&\quad (EtO)_3Si-PCL-PFPE-PCL-Si(OEt)_3 + 6\ H_2O\\&\quad \rightarrow (HO)_3Si-PCL-PFPE-PCL-Si(OH)_3 + \equiv 6\ EtOH\\&\quad \equiv Si-OH + HO-Si\equiv \rightarrow \equiv Si-O-Si\equiv +H_2O\end{aligned}$$

The final organic/inorganic (PCL–PFPE–PCL/SiO_2) weight ratio ranged from 5:95 to 20:80 as reported in Table 1.

2.3. Preparation and characterization of the coatings

Spin-coating was carried out by using a Laurell WS-400B-NPP-Lite spin-coater using a microscope glass as a support and a spin rate of 1000 rpm during 1 min. Manual dip-coating was carried out by immersion in the sol–gel solution of a microscope glass followed by its slow manual extraction (in about 10 s).

Contact angle measurements were carried out by using a DataPhysics OCA 20 apparatus. In order to avoid any surface contamination, all specimens were washed with THF and accurately dried just before measurement. Static contact angle determinations were carried out on two different specimens of the same sample and an average value of contact angle was determined on the basis of at least 20 measurements. The probe liquids were water, *n*-hexadecane, diiodomethane and dimethyl formamide. Surface tension values were determined by applying the Owens and Wendt method [18] on static contact angle values.

Atomic force microscopy (AFM) was carried out by using Park AUTOPROBE CP instrument to determine the values of RMS roughness and of the ratio between surface and projected areas.

XPS measurements were carried out on the vacuum-side surface using a Phi 15-255G double pass cylindrical mirror analyser driven in retarding mode at constant pass energy. The Mg $K\alpha_{1.2}$ line from a Vacuum Generators XR3 dual anode X-ray tube was used as the source, operated at 240 W (15 kV and 16 mA). Overview scans were taken with a pass energy of 100 eV. Higher resolution spectra of fluorine 1s (F_{1s}), silicon 2p (Si_{2p}), carbon 1s (C_{1s}) and oxygen 1s (O_{1s}) core levels were acquired for each sample with a pass energy of 50 eV. The spectra are angle integrated and they are reported in binding energy, referenced to the C–H core level component at 285.0 eV. Care was taken in order to limit the irradiation damage of the polymeric surfaces, which is known to be relevant on PFPE surfaces [9]. For this reason the acquisition times were minimised to reduce the X-ray dose on the sample. Within the acquisition times used in this work, no appreciable spectral variation could be observed.

Table 1
Composition of TXCL(*x*)Si/SiO_2 hybrids

Code	Organic–inorganic weight ratio	PFPE segments content (wt%)
TXCL(2)Si/SiO_2 5:95	5:95	3.5
TXCL(2)Si/SiO_2 10:90	10:90	7.0
TXCL(2)Si/SiO_2 20:80	20:80	14.1
TXCL(5)Si/SiO_2 5:95	5:95	2.8
TXCL(5)Si/SiO_2 10:90	10:90	5.6
TXCL(5)Si/SiO_2 20:80	20:80	11.3

3. Results and discussion

3.1. Contact angle measurements

In order to have a preliminary surface characterization (in terms of hydrophobicity and lipophobicity) of the hybrids applied by both spin- and dip-coating, static contact angles were determined by using water and *n*-hexadecane as probe liquids. For the first set of samples, the reaction time of the sol–gel process before coating application (t_r) was fixed at 3 h, according to the procedure previously adopted [17]. For comparison, contact angles of glass substrates uncoated and coated with non-fluorinated hybrids (PCLSi/SiO_2 20:80) and with completely inorganic materials (SiO_2, from TEOS) were also reported. From these data a marked increase of both water and *n*-hexadecane contact angles was observed when PFPE-based hybrids were used as coatings. However the data reported in Table 2 showed that hybrids applied by manual dip-coating were highly hydrophobic and lipophobic (water contact angles: $\theta_{H2O}=100–105°$ and *n*-hexadecane contact angles: $\theta_{HEXA}=61–68°$) while the same materials deposited by spin-coating showed significantly higher wettability with both probe liquids.

It is well evident that the method of coating application represents an important parameter to control the surface segregation of PFPE segments. In fact, a strong difference between water and *n*-hexadecane contact angle values was noted for the same type of hybrid applied by spin-coating or by dip-coating. In this respect, the thinner wet film and therefore the faster solvent volatilization in the case of spin-coating tend

Table 2
Static contact angles with water (θ_{H2O}) and *n*-hexadecane (θ_{HEXA}) for hybrids applied by spin-coating and manual dip-coating (reaction time of the sol–gel process before coating application: $t_r=3$ h)

Code	Coating method	θ_{H2O} (°)	θ_{HEXA} (°)
TXCL(2)Si/SiO_2 5:95	Spin	74.2	55.5
	Dip	104.9	63.5
TXCL(2)Si/SiO_2 10:90	Spin	75.7	58.8
	Dip	104.8	64.3
TXCL(2)Si/SiO_2 20:80	Spin	80.6	62.5
	Dip	106.5	67.6
TXCL(5)Si/SiO_2 5:95	Spin	76.6	55.7
	Dip	104.4	61.1
TXCL(5)Si/SiO_2 10:90	Spin	–	–
	Dip	104.9	65.6
TXCL(5)Si/SiO_2 20:80	Spin	83.1	63.3
	Dip	100.5	66.9
PCLSi/SiO_2 20:80	Dip	60.8	27.2
SiO_2, from TEOS	Dip	57.0	24.4
Glass substrate	–	37.4	12.9

to limit the surface segregation of PFPE segments and thus to increase the wettability with respect to the two probe liquids.

In order to verify the effect of the method of coating application combined with the progress of the sol–gel reaction, a further set of samples were deposited on glass substrates only by spin-coating with a shorter reaction time before coating application ($t_r = 1$ h).

In fact, the surface segregation of PFPE segments is expected to depend on the chain mobility of TXCL(*x*)Si and on the viscosity of the medium, and therefore on the time of reaction before coating application. Taking into account the rapid solvent volatilization which occurs immediately after the deposition of the sol–gel solution onto the substrate, a reduction of the extent of the reaction at the time of application of the solution to the substrate and an increase of the time to gel-point are expected by reducing t_r. As a consequence for $t_r = 1$ h the TXCL(*x*)Si chains can more easily move towards the surface inducing a modification of the wettability of the material. The prepared hybrids were characterized by measuring the static contact angle values by using different probe liquids and the results are reported in Table 3.

Contrary to previous results obtained for the same type of hybrids deposited by manual dip-coating (even if with different organic contents and t_r values, respectively in the ranges 20–80 wt% and 3–72 h) [17], it is very interesting to note that in the present case (spin-coating) the reaction time before coating application t_r strongly affected the surface segregation of the fluorinated segments. In fact, a marked increase of both water and *n*-hexadecane contact angles was clearly evident by decreasing t_r as can be noted by comparing the values related to spin-coated samples reported in Tables 2 and 3. From these data it is clearly evident that the extent of reaction reached by the hybrid at the moment of the coating application (and the subsequent solvent evaporation) represents a key parameter to control the chain mobility and thus the extent of the surface segregation which in turn influences the wettability behaviour.

For sake of completeness, it must be remembered that not only chemical surface composition but also surface roughness may be a key parameter for the development and control of hydrophobic and oleophobic surfaces. For this, it is important to point out that a preliminary characterization of surface morphology was carried out by atomic force microscopy which showed that all the prepared coatings were characterized by the presence of very smooth surfaces with RMS roughness values lower than 10 nm, independently by the operative conditions (spin-coating or dip-coating, organic–inorganic ratio, type of organic oligomer). In this respect, contact angle measurements can be considered completely unaffected by the surface roughness of the hybrids and thus this parameter was not reported for each sample and neglected in the discussion.

Table 3
Static contact angle (CA) data for hybrids applied by spin-coating (θ_{H2O}, CA with water; θ_{HEXA}, CA with *n*-hexadecane, θ_{DMF}, CA with dimethyl formamide; θ_{CH2I2}, CA with diiodomethane; reaction time of the sol–gel process before coating application, $t_r = 1$ h)

Code	θ_{H2O} (°)	θ_{HEXA} (°)	θ_{DMF} (°)	θ_{CH2I2} (°)
TXCL(2)Si/SiO$_2$ 5:95	109.7	67.0	99.7	93.4
TXCL(2)Si/SiO$_2$ 10:90	107.9	66.4	98.1	93.4
TXCL(2)Si/SiO$_2$ 20:80	109.2	66.7	97.8	94.8
TXCL(5)Si/SiO$_2$ 5:95	108.0	66.2	88.2	93.6
TXCL(5)Si/SiO$_2$ 10:90	107.2	66.5	89.1	93.0
TXCL(5)Si/SiO$_2$ 20:80	106.6	66.8	84.7	91.6

To conclude, it can be summarized that hybrid materials deposited by spin-coating with a short reaction time before coating application evidenced a very high hydrophobic and lipophobic character as shown by water and *n*-hexadecane contact angles whose values ranged from 100 to 107° (θ_{H2O}) and from 66 to 67° (θ_{HEXA}), respectively. In this case the surface segregation of PFPE segments appeared very high and the influence of bulk organic–inorganic ratio was almost negligible because of the strong driving force to PFPE segments surface segregation due to their very low surface tension values. In other words, even coatings with a relatively low content of organic fluorinated phase were able to lead to surfaces with similar hydrophobic and oleophobic character of organic-rich hybrids. Data indicated that the driving force for the surface segregation of the PFPE segment, expected on the basis of the low surface tension of PFPE, was almost independent on the bulk concentration of organic and inorganic components of the coating.

The surface segregation of fluorinated segments can derive from different contributions, namely by translational and segmental mobilities. The former can be limited by any kind of hindrances that in the present study may derive from both covalent and hydrogen bonding between PCL segments and silica domains but also from phase segregation of hydrogenated and fluorinated domains of the organic copolymer. With respect to this last point, it is worth noting that the length of the PCL segment represent a very important parameter for the crystallization capability of PCL segments in TXCL(*x*)Si copolymers [17]. In this view, the results obtained for spin-coated samples at different reaction times before application can be explained taking into account that by increasing the time of the sol–gel reaction before coating application there is a reduction in the translational mobility contribution. However, the main contribution to decreasing wettability is probably derived by the segmental mobility of the PFPE segments, as it is suggested by the comparison of the data for TXCL(*x*)Si/SiO$_2$ and PCLSi/SiO$_2$ reported in Table 2. In the same way it is possible to explain the difference between dip-coated and spin-coated samples; in fact the much faster solvent evaporation during spin-coating lead to a faster increasing of viscosity and possibly also to phase separation of PCL domains which may depress the translational mobility of the TXCL(*x*)Si chains.

In order to obtain a more complete surface characterization, surface tension values of the prepared coatings were determined in terms of dispersive and polar components (Table 4) by applying the Owen–Wendt method to the static contact angle values reported in Table 3.

Very low values of surface tension were measured in all cases with values ranging from 13.2 to 15.5 mN m^{-1}, according to previously published results for systems

Table 4
Total surface tension (γ) and polar (γ^p) and dispersive (γ^d) components for hybrids applied by spin-coating (reaction time of the sol–gel process before coating application: $t_r = 1$ h)

Code	γ (mN m^{-1})	γ^d (mN m^{-1})	γ^p (mN m^{-1})
TXCL(2)Si/SiO$_2$ 5:95	13.2	11.9	1.3
TXCL(2)Si/SiO$_2$ 10:90	13.5	11.9	1.6
TXCL(2)Si/SiO$_2$ 20:80	13.2	11.7	1.5
TXCL(5)Si/SiO$_2$ 5:95	14.6	12.2	2.4
TXCL(5)Si/SiO$_2$ 10:90	14.7	12.2	2.4
TXCL(5)Si/SiO$_2$ 20:80	15.5	12.6	2.9
SiO$_2$, from TEOS	42.5	22.6	19.9

constituted by PFPE segments bonded to other polymeric structures such as polyurethanes [19].

The fundamental contribution of PFPE segments on these very low values of surface tension was clearly evidenced by the results obtained for completely inorganic reference materials (obtained by using only TEOS as starting reactant) which showed a surface tension value of 42.5 mN m^{-1}, together with an important contribution due to the polar component γ^p (19.9 mN m^{-1}).

It is interesting to note that the typical value of surface tension for Fluorolink® E is 23 mN m^{-1} [20] while for fully fluorinated PFPE (i.e. fluorinated even in the terminal groups) with comparable molecular weight (about 2000 g/mol^{-1}) is about 15 mN m^{-1} [4], suggesting that the 'very surface' was composed almost completely by PFPE segments.

Data reported in Table 4 also indicated that γ values were almost independent from the organic–inorganic ratio according to the previously discussed results on wettability (water and *n*-hexadecane contact angles). The relative content of PFPE and PCL segments seems to have a slight effect as shown by the higher γ values related to TXCL(5)Si-based hybrids with respect to TXCL(2)Si counterpart, indicating that the higher polar character of PCL segments tends to increase the surface tension of the hybrids. On the other hand, also other parameters could affect the surface composition of the coating. As discussed above, the driving force for the TXCL(x)Si translation to the surface is expected to decrease by increasing the PCL segment length because of the increased molecular weight of the organic oligomer, the stronger hydrogen bonding with the more polar silica network and the more probable phase separation of PCL domains. These phenomena, in addition to the decreased PFPE/PCL ratio in the organic oligomer, can be considered responsible for the slight increase of surface tension of hybrids prepared from TXCL(5)Si with respect to TXCL(2)Si-based coatings.

3.2. XPS measurements

Contact angle measurements reflect the characteristics of the interface between the coating and the probe liquid, including both thermodynamic interactions and surface roughness. Thermodynamic interactions are related to the composition of the very surface (few angstroms) but contact angle analysis does not give direct information about type and relative concentration of different atoms, therefore an independent evaluation of surface characteristics of the hybrid materials was obtained by XPS analysis in order to investigate the composition of the outermost layer (2–3 nm) of the coatings in high vacuum atmosphere.

In Fig. 1 a typical XPS overview scan, taken on the TXCL(2)Si/SiO$_2$ 10:90 sample, is shown. Photoemission peaks form F$_{1s}$, O$_{1s}$, C$_{1s}$ and Si$_{2p}$ core levels are observed together with Auger structures related to the carbon, oxygen and fluorine elemental species. In order to get more quantitative information, higher resolution spectra in the regions of F$_{1s}$, O$_{1s}$, C$_{1s}$ and Si$_{2p}$ core levels were measured. They are reported in Fig. 2 after the subtraction of a Shirley type background.

Quantitative surface analysis can be derived from photoionization peak areas (I) of C, O, Si and F through empirical 'atomic sensitivity factors' (ASF). The relative atomic concentration of i element (C_i) can be calculated using the equation:

$$C_i = \frac{I(i)/\mathrm{ASF}(i)}{\sum_j I(j)/\sum_j \mathrm{ASF}(j)}$$

The values of ASF have to be applied accordingly to the specific instrument used and a list of such values valid for the double-pass cylindrical-mirror analyzer supplied by physical electronics has been referred to [21]. The ASF values provided in the software supplied by Phi for C$_{1s}$, O$_{1s}$, Si$_{2p}$ and F$_{1s}$ are 0.205, 0.63, 0.17 and 1.00, respectively.

The atomic surface composition (C, O, Si and F) of hybrids applied by spin-coating compared to the bulk compositions (calculated from stoichiometry) are reported in Table 5. The surface content of C and F atoms was always significantly higher than that of the corresponding bulk concentrations, indicating a strong surface enrichment of organic phase with respect to the inorganic silica phase (Si and O atoms). It could be noted that the higher surface fluorine enrichment was shown by hybrids based on TXCL(2)Si oligomers, while a different organic–inorganic ratio seems to have only a slight effect on the surface segregation, in agreement with the above discussed contact angles data.

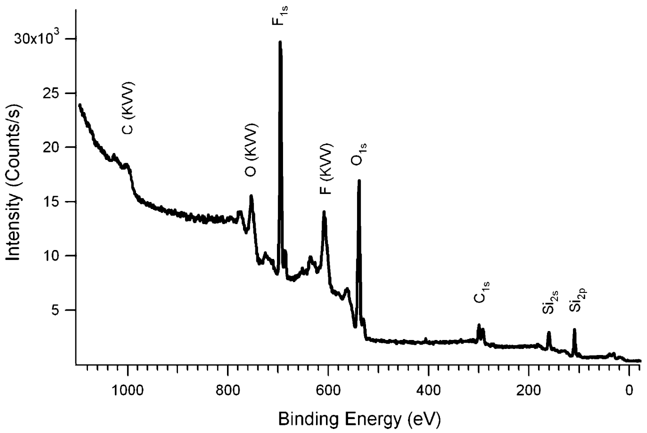

Fig. 1. XPS overview scan of TXCL(2)Si/SiO$_2$ 10:90 hybrid applied by spin-coating (reaction time of the sol–gel reaction before coating application: $t_r =$ 1 h).

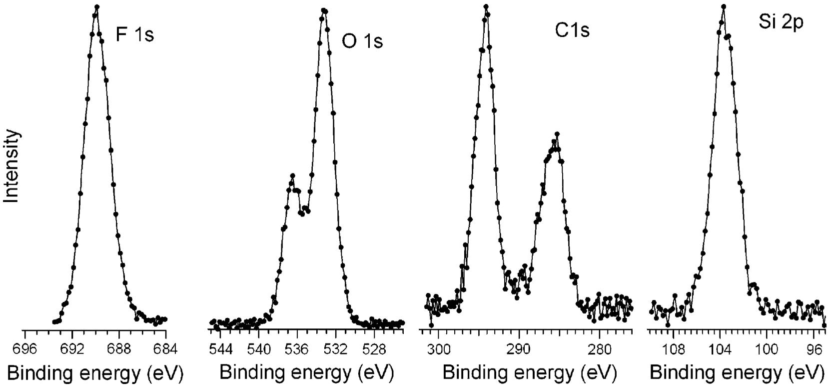

Fig. 2. XPS spectra in the regions of F_{1s}, O_{1s}, C_{1s} and Si_{2p} core levels of TXCL(2)Si/SiO_2 10:90 hybrid applied by spin-coating (reaction time of the sol–gel reaction before coating application: $t_r = 1$ h).

Further information can be obtained from the same spectra taking into account that C_{1s} and O_{1s} peaks reveal multiple components, which can be associated to atoms in different chemical states within the surface layer. In particular, C_{1s} levels exhibit two prominent features. On the basis of the comparison with a preceding work [9], the structure centered at about 295 eV is ascribed to carbon atoms bonded to fluorine atoms in the PFPE segment, while the structure centered at about 286 eV is associated to the organic hydrogenated blocks. Concerning O_{1s}, a double peaked structure is also observed. The higher binding energy component at 536.5 eV is associated to oxygen atoms in the PFPE segments and the more prominent structure at about 533.0 eV is related to the PCL segments and to oxygen atoms in the SiO_2 matrix. By evaluating the overall area subtended by the carbon atoms related to PFPE and PCL segments, the atomic ratio between carbon atoms linked to fluorine atoms (C_F) and carbon atoms linked to hydrogen atoms (C_H) can be calculated. These data are summarized in Table 6.

In order to obtain more quantitative information on the relative concentration of PFPE segments at the surface with respect to the bulk nominal concentration, and hence to derive information on the fluorinated segments segregation at the surface, the O_{1s} signal was deconvoluted into Voigt components. The O_{1s} spectra were fitted with two Voigt peaks (Lorentian FWHM = 0.2 eV, Gaussian FWHM = 2.2 eV), following the scheme proposed in a previous paper [9] for the peak assignment of oxygen in the PFPE and PCL blocks. Best fit results are shown in Fig. 3 for the TXCL(2)Si/SiO_2 10:90 sample. While the oxygen component attributable to the PFPE segments (O_{CF2}) can be clearly identified at higher binding energy (536.3 eV), different types of oxygen atoms contribute to the most pronounced peak centered at 533.1 eV. Namely, this is associated to oxygen atoms linked to Silicon (O_{Si}), which give the main contribution, and to a minor extent to oxygen singly bound to carbon (present both in PCL and in Fluorolink® E structures) and to oxygen double bonded to Carbon in PCL (only present in PCL structures). For simplicity, these last contributions were not reported in Fig. 3.

Table 5
Elemental atomic composition by XPS analysis and in bulk (in bracket, calculated from stoichiometry) for hybrids applied by spin-coating (reaction time of the sol–gel process before coating application: $t_r = 1$ h)

Code	C	O	F	Si
TXCL(2)Si/ SiO_2 10:90	21.9 (4.7)	30.9 (61.4)	32.9 (4.2)	14.3 (29.5)
TXCL(2)Si/ SiO_2 20:80	22.2 (9.3)	31.2 (56.5)	31.4 (8.3)	15.2 (25.9)
TXCL(5)Si/ SiO_2 5:95	22.1 (3.0)	34.5 (63.9)	27.5 (1.6)	15.9 (31.3)
TXCL(5)Si/ SiO_2 10:90	22.9 (5.8)	34.2(61.4)	27.1 (3.4)	15.8 (29.4)
TXCL(5)Si/ SiO_2 20:80	22.3 (11.5)	36.7 (56.2)	23.3 (6.8)	17.7 (25.5)

In Table 6 the area ratios between the O_{CF2} component (related to the organic phase) and the remaining components (O_{Si}) is reported. It can be seen that these values are largely higher than those expected for the bulk composition, even though this evaluation overestimates the relative concentration of inorganic phase because the O_{Si} peak also contains peaks attributable to other hydrogenated organic segments. This clearly indicates a segregation of the organic phase at the surface.

It is noteworthy that in all investigated samples, the most prominent peak at 533.1 eV appears less intense than would be expected considering the Si_{2p} measured intensity and calculating the expected value of the O_{Si} peak in the SiO_2 using the appropriate ASF for the used instrument [21]. This can be

Table 6
XPS analysis after peak deconvolution for hybrids applied by spin-coating (reaction time of the sol–gel process before coating application: $t_r = 1$ h)

	O_{CF2}/O_{Si}		C_F/C_H	
Code	Bulk[a]	Surface[b]	Bulk[a]	Surface[b]
TXCL(2)Si/SiO_2 10:90	0.03	0.47	0.80	1.38
TXCL(2)Si/SiO_2 20:80	0.06	0.38	0.80	1.20
TXCL(5)Si/SiO_2 5:95	0.01	0.28	0.42	0.79
TXCL(5)Si/SiO_2 10:90	0.02	0.30	0.42	0.98
TXCL(5)Si/SiO_2 20:80	0.05	0.22	0.42	0.60

C_F/C_H, atomic ratio between C atoms linked to F atoms and C atoms linked to H atoms; O_{CF2}/O_{Si}, atomic ratio between O atoms linked to $–CF_2–$ groups and O atoms linked to Si atoms.

[a] From stoichiometry.

[b] From XPS analysis.

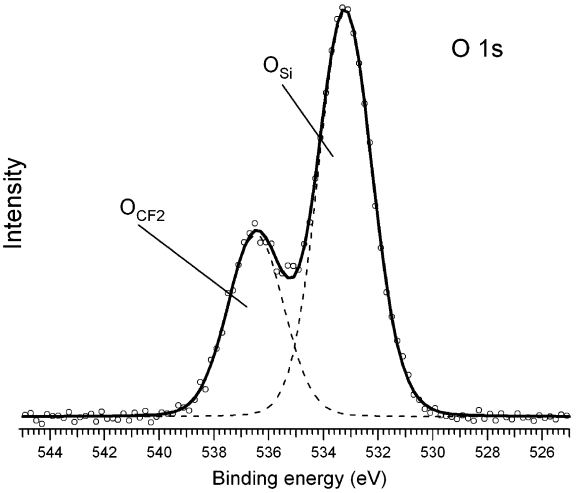

Fig. 3. Best fit of O_{1s} XPS signal deconvoluted into Voigt components for TXCL(2)Si/SiO_2 10:90 hybrids applied by spin-coating (reaction time of the sol–gel reaction before coating application: $t_r = 1$ h).

qualitatively understood considering the different escape depth of O_{1s} and Si_{2p} electrons excited by Mg K_α radiation [22] and the resultant higher relative attenuation of the O_{Si} with respect to the Si_{2p} electrons from the enriched organic surface layer.

As demonstrated by the results obtained by contact angle and XPS analysis, all the investigated samples showed a very strong surface segregation in organic segments as evidenced by comparing the values corresponding to the bulk composition (calculated from stoichiometry) and the surface composition (determined from XPS analysis). The PFPE surface enrichment ranged from 5 to 30 times with respect to the bulk composition.

On the other hand, XPS measurements allow to derive more information about the presence in the very surface of perfluorinated and hydrogenated organic blocks. In fact, assuming the completion of the sol–gel reaction and thus that all alkoxysilane groups (mainly deriving from TEOS but also from TXCL(*x*)Si organic oligomer) were converted into silica groups, the C_F/C_H atomic ratio describes the relative content of perfluorinated PFPE segments and of other hydrogenated organic segments (mainly PCL). Also in this case all the samples showed a C_F/C_H atomic ratio significantly higher at the surface than that expected for the bulk indicating that the thermodynamic driving force of PFPE segments to segregate at the interface between air and coating (related to their very low values of surface energy) tends to displace preferably PFPE segments at the very surface. This conclusion is further supported taking into account that the reported C_F/C_H atomic ratio at the very surface may be underestimated due to hydrocarbon contamination which generally increase the C_H content in the XPS analysis.

4. Conclusions

Perfluoropolyether-based organic–inorganic hybrids were prepared by sol–gel process and applied onto glass substrates by both dip-coating and spin-coating. Hydrophobic and lipophobic character (evaluated by measuring the contact angle with water and *n*-hexadecane) was very high for all the prepared samples, almost independent by the organic/inorganic ratio. The wettability with polar and apolar liquids decreased by using the dip-coating technique instead of the spin-coating one and by decreasing the reaction time of the sol–gel process before coating application. Very low values of surface tension were determined, indicating a strong surface segregation of PFPE segments. All these effects can be explained by assuming that both segmental mobility of PFPE segments and translational mobility of TXCL(*x*)Si chains contribute to give fluorine-rich surfaces. These evidences were further supported by XPS analysis which showed an interface between air and coating with an organic/inorganic ratio much higher than that expected from bulk composition and with a preferential surface segregation of PFPE segments also with respect to the other hydrogenated organic segments.

All the presented data seem to suggest that the most important contribution to the surface segregation of fluorinated organic oligomers was the segmental mobility, even though the translational mobility, which depends on several factors (i.e. covalent and hydrogen bonding between PCL segments and silica domains and possible phase separation of hydrogenated and fluorinated domains of the organic copolymer, etc.), may give a significant contribution. In this respect, the translational contribution can be increased by optimizing operative conditions such as time of the sol–gel reaction before coating application and/or coating application technique.

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