Surface Properties of Fluorinated Hybrid Coatings

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ABSTRACT: A commercial perfluoropolyether containing alkoxysilane functionalities was employed to prepare organic–inorganic hybrid coatings by using the sol-gel process in the presence of tetraethoxysilane. Contact angle analysis revealed a strong hydrophobic and oleophobic character of the coatings almost independently from the molecular weight of the starting fluorinated oligomer. Surface tension values were in the range of 14–16 mN/m, suggesting a preferential segregation of fluorinated segments onto the surface of the coating. Atomic force microscopy showed the presence very smooth surfaces permitting to neglect the contribution of the surface roughness to wettability. Friction coefficient values were markedly lower with respect to the value of uncoated glass substrate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1483–1488, 2006

Key words: coatings; surfaces; fluoropolymers

INTRODUCTION

Organic–inorganic nanocomposites can be defined as heterogeneous materials with organic and inorganic phases intimately mixed where at least one of the components' domains has a dimension ranging from some Angstrom to several nanometers. These kind of nanocomposites are increasingly important materials because of their extraordinary properties deriving from the synergism between the properties of each individual component.[1,2] Actually, the combination at the nanosize level of inorganic and organic components in a single material has made accessible an immense new area of materials science that has extraordinary implications in the development of multifunctional materials.

Organic–inorganic hybrids can be subdivided according to the nature of their interface: the material can be classified as *class I* hybrid if the organic and inorganic components are simply embedded and only weak bonds (van der Waals, ionic, or hydrogen bonds) are present at the interface; on the opposite, *class II* hybrids are materials in which the organic and inorganic phases are linked together by strong covalent or ion-covalent bonds.

These materials have gained much interest because of the remarkable change in properties such as mechanical, thermal, electrical, and magnetic when compared with that of pure organic polymers. Several applications have been already developed for this kind of hybrid materials,[3] in particular in the field of protective coatings of both organic and inorganic substrates.

All the different approaches that can be used to prepare these materials refer to the following two main strategies: (a) assembling (or self-assembling) or dispersion of well-defined nanobuilding blocks, which consist of perfectly calibrated preformed objects that keep their integrity in the final material[4] and (b) synthesis based on very convenient soft chemistry including conventional sol–gel chemistry, the use of specific bridged and polyfunctional precursors, and hydrothermal synthesis.[1]

Thanks to its mild operative conditions, the most commonly employed preparation procedures are based on the sol–gel process,[5] which lead to the formation of the inorganic network by starting from liquid precursors such as metal alkoxides and organic oligomers preferably with suitable reactive groups. In fact, the covalent bonding between organic and inorganic components (*class II* hybrids) can lead to the formation of a crosslinked structure in which the organic and inorganic moieties are phase separated on a micro- or nanoscale, but the resulting material is macroscopically uniform.

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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),[6,7] which presents the typical properties of fluoro-products.[8] In particular, PFPE 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 oleophobicity, and in particular very low surface energy, with values varying in the range 14–25 mN/m depending on the molecular weight.

In previous works, because of the marked thermodynamic incompatibility of pure PFPE with the chemicals and solvents commonly used in sol–gel processes, PFPE oligomers were modified by preparing block copolymers containing polycaprolactone segments,[9] leading to an organic material with improved solubility. The PFPE segments present in the prepared poly(caprolactone-b-PFPE-b-caprolactone) (PCL–PFPE–PCL) triblock copolymers tend to migrate to the outer surface as a consequence of the strong thermodynamic driving force to minimize the surface energy.[10,11] The same behavior was also noted in the case of polymer blends,[12,13] and thus, a similar mechanism of surface segregation can be in principle expected in the case of hybrid systems containing PFPE segments.

In a previous study, we already reported the preparation[14] and the surface characterization[15,16] (in terms of contact angle and XPS measurements) of organic–inorganic hybrid coatings by using the sol–gel process and alkoxysilane-terminated PCL–PFPE–PCL block copolymers and tetraethoxysilane (TEOS) as starting materials. The wettability and the surface composition 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 enough to give a very high hydrophobic character to the coating surface.

These organic–inorganic hybrid materials can be potentially used as functional coatings to prepare hydrophobic–oleophobic coatings for several substrates. To our knowledge, the use of PFPE for the preparation of ceramers by using the sol–gel process was only reported by Wojcik and Klein[17] 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–oleophobic materials obtained by sol–gel approach.[18–24]

The recent commercial availability of PFPE containing alkoxysilane functionalities[25] made possible their direct use as organic precursor for organic–inorganic hybrids. Of course the possibility to use a commercial product can be of great interest with respect to materials such as the above described alkoxysilane-terminated PCL–PFPE–PCL block copolymers only produced in a laboratory scale.

On the basis of these considerations, in the present study we investigated the surface properties of these kind of PFPE-based nanocomposites by using TEOS as inorganic network former.

EXPERIMENTAL

Materials

α,ω-Triethoxysilane terminated PFPE was supplied by Solvay Solexis under the trade name Fluorolink® S 10. Three different grades with molecular weight of $\sim$1100, 1550, and 2000 g/mol, respectively, were specifically prepared by Solvay Solexis for this study. The materials were coded as FS10-x in which x represents the molecular weight of the oligomer. The molecular structure of Fluorolink S 10 can be represented as follows:

$$(EtO)_3Si–CH_2CH_2CH_2–NH–CO–CF_2O(CF_2CF_2O)_m$$

$$(CF_2O)_nCF_2–CO–NH–CH_2CH_2CH_2–Si(OEt)_3$$
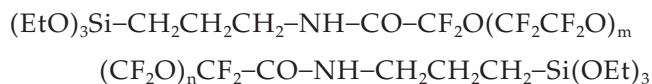
Tetraethoxysilane (TEOS, purchased from Aldrich), tetrahydrofuran (THF, Carlo Erba) ethanol (EtOH, Carlo Erba), and hydrochloric acid at 37% concentration (Carlo Erba) were high purity reagents and were used as received without further purification.

Preparation of organic–inorganic hybrids

FS10-x/TEOS mixtures were dissolved in THF at a concentration of about 20% w/v and 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 FS10-x and TEOS): EtO-:EtOH:H$_2$O:HCl = 1:1:1:0.05.

A typical preparation was as follows: 2.0 g of a FS10-x/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 ($t_r = 0$, 30, and 60 min) to allow a partial progress of the sol–gel reaction. Then the sol–gel solution was deposited by spin-coating onto microscope glasses previously cleaned by washing in standard RCA1 solution (NH$_4$OH:H$_2$O$_2$:H$_2$O = 1:1:5) and rinsed in bi-distilled water. After a period of 5 min at room temper-

TABLE I
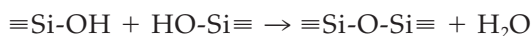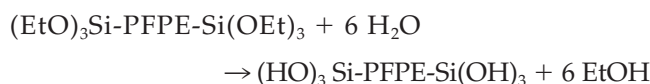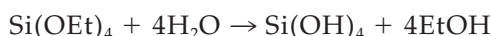**Static Contact Angles with Water ($\theta_{\text{H}_2\text{O}}$) and n-Hexadecane ($\theta_{\text{HEXA}}$)**

Code	t_r (min)	$\theta_{\text{H2O}} \pm$ SD (°)	$\theta_{\text{H2O}}{}^a \pm$ SD (°)	$\theta_{\text{HEXA}} \pm$ SD (°)
FS10–1100/SiO$_2$ 10/90	0	108.3 ± 0.5	106.5 ± 0.6	65.8 ± 0.3
	30	104.4 ± 0.4	104.8 ± 0.7	64.2 ± 0.6
	60	104.6 ± 0.5	104.0 ± 0.7	64.5 ± 0.4
FS10–1550/SiO$_2$ 10/90	0	108.3 ± 0.8	107.9 ± 0.7	67.0 ± 0.2
	30	103.8 ± 0.8	102.8 ± 0.8	65.1 ± 0.3
	60	107.9 ± 0.5	107.9 ± 1.0	66.8 ± 0.4
FS10–2000/SiO$_2$ 10/90	0	112.4 ± 0.4	109.9 ± 0.6	68.5 ± 0.2
	30	106.1 ± 0.9	104.1 ± 1.1	65.0 ± 0.3
	60	109.0 ± 0.5	106.0 ± 0.4	67.0 ± 0.3
SiO$_2$, from TEOS	0	57.0 ± 0.8	ND	24.4 ± 0.7
Glass substrate	—	37.4 ± 2.7	ND	12.9 ± 3.1

t_r, time of the sol–gel reaction before coating application; SD, standard deviation.
[a] After 30 min immersion in THF.

ature, samples were subjected to a thermal post-treatment at 100°C for 2 h.

The final organic/inorganic weight ratio was calculated by assuming the completion of the sol–gel reactions reported below and was kept equal to 10:90:

$$Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 + 4EtOH$$

$$(EtO)_3Si\text{-PFPE-}Si(OEt)_3 + 6\,H_2O$$
$$\rightarrow (HO)_3\,Si\text{-PFPE-}Si(OH)_3 + 6\,EtOH$$

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$$

Characterization

Spin-coating was carried out by using a Laurell WS-400B-NPP-Lite spin-coater using a spin rate of 1000 rpm during 1 min. The spin-coating process was carried out at room conditions (20–25°C, 35–55% relative humidity).

Contact angle measurements were carried out by using a DataPhysics OCA 20 apparatus. To avoid any surface contamination, all specimens were completely immersed in THF (for 1 or 30 min, to verify the coating stability) and accurately dried just before measurement. Static contact angle was measured 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 and n-hexadecane. Surface tension was determined by applying the Owens and Wendt method[26] on static contact angle values.

Atomic force microscopy (AFM) was carried out by using a Park AUTOPROBE CP instrument operating in noncontact mode

Friction coefficient was determined through scratch tests carried out on a CSM Micro-Combi Tester by using a Rockwell C diamond scratch indenter ($R = 800$

μm) and a constant load of 100 mN for a scratch length of 1 mm.

RESULTS AND DISCUSSION

Contact angle measurements

To have a preliminary surface characterization in terms of hydrophobicity and oleophobicity of the hybrids applied by spin-coating, static contact angles were determined by using water and n-hexadecane as probe liquids. The reaction time of the sol–gel process before coating application (t_r) was varied from 0 to 60 min to verify the effect of the extent of the reaction (i.e., the degree of crosslinking of the hybrid structure) on the translational mobility of FS10-x, which in turn can be considered one of the main contributions to the surface segregation of the low surface tension PFPE segments.

Data reported in Table I showed that all hybrids of the series FS10-x/SiO$_2$ 10/90 were highly hydrophobic and oleophobic (water contact angles: $\theta_{\text{H2O}} = 104$–112° and n-hexadecane contact angles: $\theta_{\text{HEXA}} = 64$–68°) without any evident correlation with both the molecular weight of the organic oligomer and the time of the sol–gel reaction before coating application. Data demonstrated that the driving force to surface segregation of PFPE segments (due to their low surface tension) was high enough to lead to a fluorine surface enrichment at the very surface of the coating and that the PFPE segments mobility responsible for this preferential segregation was practically unaffected by the above said parameters.

Furthermore, the coating stability was checked by repeating the water contact angle measurements after the sample immersion in tetrahydrofuran for 30 min. Data reported in Table I (column) showed that contact angles did not change with respect to the values recorded immediately after coating preparation (third

TABLE II
Total Surface Tension (γ) and Polar (γ^p) and Dispersive (γ^d) Components

Code	t_r (min)	γ (mN/m)	γ^d (mN/m)	γ^p (mN/m)
FS10–1100/SiO$_2$ 10/90	0	15.0	13.7	1.3
	30	16.2	14.2	2.0
	60	16.1	14.1	2.0
FS10–1550/SiO$_2$ 10/90	0	14.7	13.3	1.4
	30	16.1	13.9	2.2
	60	14.8	13.3	1.5
FS10–2000/SiO$_2$ 10/90	0	13.6	12.8	0.8
	30	15.6	13.9	1.7
	60	14.5	13.3	1.2
SiO$_2$, from TEOS	0	46.4	25.1	21.3
Glass substrate	—	59.9	26.8	33.1

t_r, time of the sol–gel reaction before coating application.

column), indicating a very good chemical resistance toward organic solvents such as tetrahydrofuran. In other words, the crosslinked structure of the hybrids with covalent bonding between organic and inorganic phases lead to the formation of a stable coating onto the glass substrate.

It is also worth to note the extremely limited standard deviation related to the contact angle measurements, indicating that all the surfaces were very homogeneous.

For comparison, contact angles of glass substrates uncoated and coated with completely inorganic materials ("SiO$_2$, from TEOS," for its preparation see reference[15]) 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, confirming the fundamental contribution to hydrophobicity and oleophobicity deriving from the fluorinated component.

To obtain a more detailed surface characterization, surface tension was determined together with their dispersive and polar components (see Table II) by

applying the Owens-Wendt method to the static contact angle values reported in Table I.

Very low values of surface tension were calculated in all cases with values ranging from 13.6 to 16.2 mN/m, according to previously published results for systems constituted by PFPE segments bonded to other polymeric structures such as polyurethanes.[27] The fundamental contribution of PFPE segments on these very low values of surface tension was clearly evidenced by comparing them with values obtained in the case of fully inorganic reference materials ("SiO$_2$, from TEOS") which showed a surface tension value of 46.4 mN/m, together with an important contribution due to the polar component γ^p (21.3 mN/m).

It is worth to note that the typical value of surface tension for Fluorolink products ranges from 22.5 to 5 mN/m,[25] while for fully fluorinated PFPE (i.e., fluorinated even in the terminal groups) with comparable molecular weight (about 2000 g/mol) is about 15 mN/m,[6] suggesting that the so-called "very surface" of the samples presented in this work was almost completely composed by PFPE segments, according to results previously reported for similar systems.[28]

Atomic force microscopy and surface morphology

It is well known that the wettability behavior of real surfaces is controlled by surface morphology other than surface chemical composition. In fact, it is well known that both surface roughness and surface heterogeneity strongly affect the contact angle measurements as pointed out by the classical studies of Wenzel[29,30] and Cassie.[31] In the so-called "Wenzel regime" ("rough regime") the surface free energy of the solid part of a rough surface is r times higher than that of a flat surface, and the hydrophobicity–oleophobicity of a rough surface is increased by the increase of the solid–liquid contact area.

AFM was carried out on the prepared coatings to evaluate the presence of a "Wenzel regime" and thus
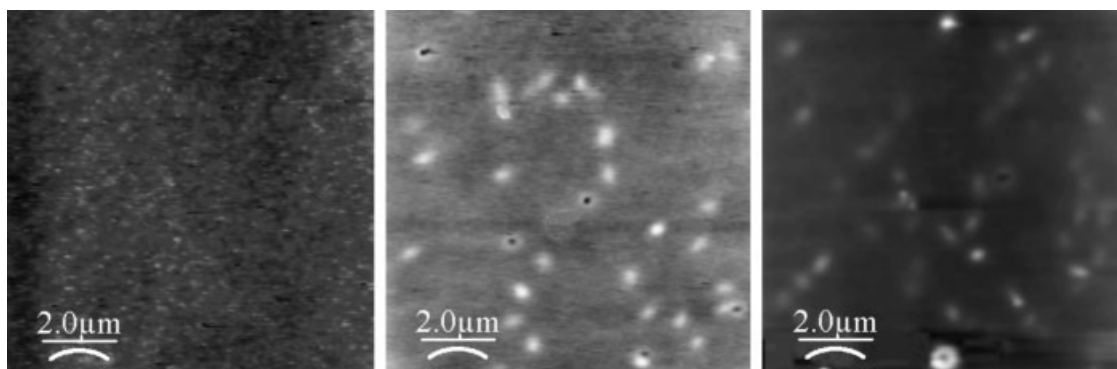

Figure 1 Typical topographic images of FS10–1100/SiO$_2$ 10/90 (a), FS10–1550/SiO$_2$ 10/90 (b), and FS10–2000/SiO$_2$ 10/90 (c) (time of the sol–gel reaction before coating application, 30 min).

the contribution of surface morphology to the wettability. Some typical topographic images are reported in Figure 1, while the values of RMS roughness and of the ratio between surface area and projected area (r, the so-called roughness factor according to the definition of Wenzel[29,30]) are reported in Table III.

Also in this case it was practically impossible to find out any correlation with both the molecular weight of the organic oligomer and the time of the sol–gel reaction before coating application. However, it is worth noting that all the prepared coatings presented a very smooth surface with RMS roughness values well below 10 nm. According to these data, also the roughness factor r was approximately unitary, indicating the absence of significant surface roughness.

On the basis of these results, the contact angle data discussed earlier can be considered completely unaffected by the surface roughness of the hybrids and thus this last parameter can be neglected for the discussion because of the absence of a "Wenzel regime". In other words, the wettability behavior of the investigated hybrids only takes its origin from the chemical surface composition and thus from the preferential surface segregation of fluorinated segments.

Scratch test and friction coefficient

Friction coefficient values (reported in Table IV) were determined with scratch tests carried out by using a scratch indenter having a tip radius of 800 μm and operating at a constant load of 100 mN for a scratch length of 1 mm.

All the prepared coatings showed friction coefficient significantly lower than that of uncoated glass substrate. These data represent a further indirect indication of the strong preferential segregation of PFPE segments onto the outer surface, which is able to transfer the peculiar properties of this type of fluorinated

TABLE IV
Friction Coefficient (*f*) Determined with Scratch Tests

Code	t_r (min)	f (10^3)
FS10–1100/SiO$_2$ 10/90	0	1.9
	30	0.7
	60	4.5
FS10–1550/SiO$_2$ 10/90	0	1.6
	30	2.2
	60	2.1
FS10–2000/SiO$_2$ 10/90	0	2.3
	30	2.5
	60	3.1
Glass substrate	—	7.7

t_r, time of the sol–gel reaction before coating application.

materials (in the specific case low friction coefficient) to the very surface of the functional coating.

CONCLUSIONS

Commercial PFPEs, named Fluorolink S 10, with different molecular weights and containing alkoxysilane end-groups were directly used to prepare organic–inorganic hybrids by sol–gel process and the resulting materials were applied onto glass substrates by spin-coating. Both hydrophobic and oleophobic characters (evaluated by measuring the contact angle with water and *n*-hexadecane) were very high for all the prepared samples, almost independently by the molecular weight of the organic fluorinated oligomer. The contact angle data and the very low values of surface tension indicated the occuring of a strong preferential segregation of PFPE segments onto the outer surface of the coatings. The wettability behavior was found to be only dependent on the surface chemical composition taking into account that the surface roughness could be neglected as evidenced by AFM. Furthermore, a significant depression of friction coefficient was observed with respect to the uncoated glass substrate.

TABLE III
RMS Roughness and Surface-Projected Areas Ratio (*r*)
Determined with Atomic Force Microscopy

Code	t_r (min)	RMS roughness (Å)	r
FS10–1100/SiO$_2$ 10/90	0	15	1.00
	30	5	1.00
	60	95	1.00
FS10–1550/SiO$_2$ 10/90	0	17	1.00
	30	12	1.00
	60	29	1.01
FS10–2000/SiO$_2$ 10/90	0	6	1.00
	30	10	1.01
	60	6	1.00

t_r, time of the sol–gel reaction before coating application.

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