Spontaneous multiscale phase separation within fluorinated xerogel coatings for fouling-release surfaces

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Four-component xerogel films consisting of 1 mole-% *n*-octadecyltrimethoxysilane (C18) and 50 mole-% tetraethoxysilane (TEOS) in combination with 1–24 mole-% tridecafluoro-1,1,2,2-tetrahydrooctyltriethoxysilane (TDF) and 25–48 mole-% *n*-octyltriethoxysilane (C8) and a 1:49:50 mole-% C18/TDF/TEOS were prepared. Settlement of barnacle cyprids and removal of juvenile barnacles, settlement of zoospores of the alga *Ulva linza*, and strength of attachment of 7-day sporelings (young plants) of *Ulva* were compared amongst the xerogel formulations. Several of the xerogel formulations were comparable to poly(dimethylsiloxane) elastomer with respect to removal of juvenile barnacles and removal of sporeling biomass. The 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogels displayed some phase segregation by atomic force microscopy (AFM) pre- and post-immersion in water. Imaging reflectance infrared microscopy showed the formation of islands of alkane-rich and perfluoroalkane-rich regions in these same xerogels both pre- and post-immersion in water. Surface energies were unchanged upon immersion in water for 48 h amongst the TDF-containing xerogel coatings. AFM measurements demonstrated that surface roughness on the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogel coatings decreased upon immersion in water.

Keywords: biofouling; macrofouling; fouling release; topography; barnacle settlement; barnacle removal; *Ulva* zoospore settlement; *Ulva* sporeling removal; xerogels; perfluoroalkyl

Introduction

Biofouling on ships' hulls is a significant problem worldwide causing an increase in fuel consumption due to drag (Schultz 2007; Schultz et al. 2011) as well as mediating the spread of non-indigenous species (reviewed by Piola et al. 2009). The economic impact of biofouling has been estimated to be \$56M per year (\$1B over 15 years) for a single class of naval vessel (Schultz et al. 2011). Biocides have been used in the past to combat biofouling, but the use of biocides in antifouling (AF) paints is becoming increasingly restricted (see Thomas and Brooks 2010).

Environmentally benign approaches to the control of biofouling integrate the biology/biochemistry of fouling and the role of surface characteristics of materials (for a review see Genzer and Efimenko 2006). The secretion, cross-linking or curing of bioadhesives produced by macrofouling organisms are areas of active research (Dickinson et al. 2009; Barlow et al. 2010; Gohad et al. 2010; Kamino 2010; Wilker 2010). Mechanisms of adhesive cross-linking/ curing include radical-mediated cross-linking, enzymecatalyzed protein modification and cross-linking, and development of specific protein hierarchical structures (eg amyloid-like fibrils). The elastic modulus of surfaces influences the detachment mechanism of fouling organisms (Ramsay et al. 2008) and artificial systems such as "pseudobarnacles" (Brady and Singer 2000; Berglin et al. 2003; Kim et al. 2007). Materials with a low elastic modulus deform readily and release fouling organisms by peeling while rigid materials release organisms by shear.

Initially, non-biocidal commercial products were based on poly(dimethylsiloxane) elastomer (PDMSE), but newer commercial products effectively utilize fluorinated groups (Dobretsov and Thomason 2011). Historically, several fluoropolymers were considered as fouling-release (FR) coatings because of their low surface energies (Lindner 1992; Davis 1996; Brady 1997). However, the fluoropolymers rapidly fouled (Davis 1996; Brady 1997) perhaps due to a combination of low surface energies outside the 20–25 mN m⁻¹ minimum range in the "Baier curve" where minimal bioadhesion has been reported (Baier et al. 1968; Baier 1984), their non-elastomeric nature, and "rough" surfaces promoting adhesive interlocking. In some experimental coatings, blends of a fluorocarbon polymer with polysiloxanes, polystyrenes, and polyethylene glycols are being investigated and provide good performance in laboratory assays (eg Gudipati et al. 2005; Marabotti et al. 2009; Martinelli et al. 2009; Weinman et al. 2009). These materials have low surface energies in the dry state, but those based on amphiphilic polymers (eg Martinelli et al. 2008, 2011; Weinmann et al. 2009) reconstruct underwater, becoming more hydrophilic. These materials have low surface energies and low elastic-moduli promoting the peeling mechanism for FR (Brady and Singer 2000).

Fluorinated FR polymers based on blends of a fluorocarbon polymer with polysiloxanes, polystyrenes, and polyethylene glycols are expensive to produce and often the coatings are constructed in layers. Organically-modified, hybrid xerogel coatings have been shown to possess AF/FR characteristics (Tang et al. 2005; McMaster et al. 2009; Bennett et al. 2010; Finlay et al. 2010), are inexpensive to produce and have been applied to surfaces via spin coating, dip coating, spray coating, and brushing (Tang et al. 2005; Selvaggio et al. 2009). These coatings have a range of surface energies and include both hydrophilic and hydrophobic surfaces. Approximately 100 boats have been coated with an organically-modified, hybrid xerogel (AquaFast[®]) and the same material has been used to minimize biofouling on the monitoring system of an underwater archaeological site (Selvaggio et al. 2009). The present authors recently described hybrid xerogel surfaces of $1-2-\mu m$ thickness and low surface energy incorporating 1 mole-% of an *n*-octadecyltrimethoxysilane (C18) precursor in combination with noctyltriethoxysilane (C8) and tetraethoxysilane (TEOS) that released juvenile barnacles and sporelings (young plants) of Ulva efficiently (Gunari et al. 2011). These coatings displayed structural features on both the micrometer and nanometer scale as observed by imaging transmission infrared (IR) microscopy and atomic force microscopy (AFM) measurements.

The incorporation of fluoroalkane functionality within xerogel coatings is straightforward with the solgel process. Mixed alkane and perfluoroalkane modifications can be incorporated from appropriate perfluoroalkyl- and alkyltrialkoxysilane precursors. In this paper, surface segregation into nm- and/or μ m-scale structural features on surfaces containing hydrocarbon and fluorocarbon functionality from xerogel coatings prepared from sol precursors incorporating 1 mole-% C18 and 1–24 mole-% tridecafluorooctyl-triethoxysilane (TDF) in combination with C8 and 50 mole-% TEOS is demonstrated. In this series, coatings with values of $\gamma_{\rm S}$ outside the 20–25 mN m⁻¹ minimal-

adhesion zone of the Baier curve behave as AF/FR coatings. The TDF-containing coatings were evaluated with respect to the impact of fluorocarbon content on the settlement of cypris larvae of the barnacle *Balanus amphitrite* and zoospores of the macrofouling algae *Ulva linza* and on the release of juvenile barnacles and sporelings of *Ulva*.

Materials and methods

Chemical reagents and materials

Deionized water was prepared to a specific resistivity of at least 18 M Ω using a Barnstead NANOpure Diamond UV ultrapure water system. Tetraethoxysilane (TEOS), *n*-octadecyl-trimethoxysilane (C18), tridecafluoro-1,1, 2,2-tetrahydrooctyltriethoxysilane (TDF), and *n*-octyltriethoxysilane (C8) were purchased from Gelest, Inc. and were used as received. Ethanol was purchased from Quantum Chemical Corp. Hydrochloric acid and isopropanol were obtained from Fisher Scientific Co. Borosilicate glass microscope slides were obtained from Fisher Scientific, Inc. Silastic[®] T2 (Dow Corning) coated slides ca 500 μ m in thickness, were provided by Dr AB Brennan, University of Florida (Schumacher et al. 2007).

Sol preparation

The sol/xerogel composition is designated in terms of the molar ratio of Si-containing precursors. Thus, a 50:50 C8/TEOS composition contains 50 mole-% C8 and 50 mole-% TEOS. In all the sol preparations described below, the aqueous HCl was added last. Unless noted otherwise, all sols were capped and stirred at ambient temperature.

50:50 C8/TEOS

A mixture of TEOS (2.09 g, 2.24 ml, 10 mmol), C8 (2.78 g, 3.16 ml, 10 mmol), isopropanol (4.0 ml), and 0.100 M HCl (1.23 ml, 0.123 mmol) was capped and stirred for 24 h. This sample, which did not contain TDF, served as a control xerogel surface.

1:1:48:50 C18/TDF/C8/TEOS

A mixture of C18 (0.135 g, 0.36 mmol), TDF (0.184 g, 0.36 mmol), C8 (4.78 g, 17.3 mmol), TEOS (3.75 g, 18.0 mmol), ethanol (8.47 ml), and 0.1 M HCl (2.27 ml), was stirred for 24 h.

1:4:45:50 C18/TDF/C8/TEOS

A mixture of C18 (0.135 g, 0.36 mmol), TDF (0.735 g, 1.44 mmol), C8 (4.48 g, 16.2 mmol), TEOS (3.75 g,

18.0 mmol), ethanol (11.9 ml), and 0.1 M HCl (2.27 ml) was stirred for 24 h.

1:9:40:50 C18/TDF/C8/TEOS

A mixture of C18 (0.135 g, 0.36 mmol), TDF (1.65 g, 3.24 mmol), C8 (3.98 g, 14.4 mmol), TEOS (3.75 g, 18.0 mmol), ethanol (11.9 ml), and 0.1 M HCl (2.27 ml) was stirred for 24 h.

1:14:35:50 C18/TDF/C8/TEOS

A mixture of C18 (0.135 g, 0.36 mmol), TDF (2.57 g, 5.04 mmol), C8 (3.48 g, 12.6 mmol), TEOS (3.75 g, 18.0 mmol), ethanol (11.5 ml) and 0.1 M HCl (2.27 ml) was stirred for 24 h.

1:19:30:50 C18/TDF/C8/TEOS

A mixture of C18 (0.135 g, 0.36 mmol), TDF (3.49 g, 6.84 mmol), C8 (2.99 g, 10.8 mmol), TEOS (3.75 g, 18.0 mmol), ethanol (11.5 ml), and 0.1 M HCl (2.27 ml) was stirred for 24 h.

1:24:25:50 C18/TDF/C8/TEOS

A mixture of C18 (0.135 g, 0.36 mmol), TDF (4.41 g, 8.64 mmol), C8 (2.49 g, 9.0 mmol), TEOS (3.75 g, 18.0 mmol), ethanol (11.5 ml), and 0.1 M HCl (2.27 ml) was stirred for 24 h.

Xerogel film formation

Prior to use, glass microscope slides (25-mm × 75mm) were soaked in piranha solution for 24 h, rinsed with copious quantities of deionized water, soaked in isopropanol for 10 min, air dried and stored at ambient temperature. Xerogel films were formed by spin casting 400 μ l of the sol precursor onto the microscope slides. A model P6700 spincoater (Specialty Coatings Systems, Inc.) was used at 100 rpm for 10 s to deliver the sol and at 3000 rpm for 30 s to coat. Profilometry indicated that the xerogel films cast in this manner were 1–2 μ m thick.

For barnacle cyprid assays, glass 20-mm × 60mm Petri dish bottoms (VWR Scientific, Inc.) were soaked in piranha solution for 24 h, rinsed with copious quantities of deionized water, and stored in an oven at 110°C until use. The Petri dish bottoms were cooled to ambient temperature and 600 μ l of the appropriate sol precursor were added. The Petri dish was manipulated until the bottom surface and ~ 5 mm of the side surface were covered. The excess sol precursor was removed *via* pipette. All coated surfaces (glass slides and Petri dishes) were dried at ambient temperature and humidity for at least 7 days prior to analysis.

Imaging reflectance infrared (IR) microscopy of xerogel samples

Imaging reflectance IR microscopy was carried out using a Bruker Vertex 70 IR coupled with a Hyperion 3000 IR microscope (4 cm⁻¹, 64 scans, 15 \times objective, 64×64 focal plane array). IR scans were collected in reflectance mode utilizing an FPA (focal plane array) detector with a detection area of 200 $\mu m \times 200 \ \mu m$. Samples of the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogel on aluminum-coated glass slides were prepared by spin casting 400 μ l of the sol precursor onto 25-mm \times 75-mm \times 1.1-mm borosilicate float glass microscope slides coated with 50 + 1 nm aluminum (Deposition Research Laboratories, Inc.) and air drying the films at ambient temperature for at least 7 days. One set of xerogel films was analyzed following air-drying while a second set of xerogel films was soaked in deionized water at 25°C for 24 h and then dried at ambient temperature and humidity for 2 h. The IR data collected for the $200 \times 200 \ \mu m$ area was baseline corrected relative to the aluminum-coated slide as a blank and then integrated over the C-H stretching region (2800- 3000 cm^{-1}) and the C-F stretching region (1223– 1275 cm^{-1}). The 2D color images of relative intensity were then converted to 32 bit black and white images using Image-J software, where the "color" intensity was converted to gray-scale intensity. The ratio of the two images (C-F/C-H) was then calculated using the Ratio Plus plugin, resulting in a single image in which black areas pertain to an enhancement of fluorocarbon signal or reduced signal pertaining to hydrocarbon species and white areas pertain to enhanced signal from hydrocarbon species or reduced signal from fluorocarbon species.

Atomic force microscope (AFM) imaging measurements

The samples were imaged by AFM using a Nanoscope[®] Dimension 3100 scanning probe microscope (Bruker AXS, Santa Barbara, CA) in an environmentally controlled laboratory with the relative humidity set at 25%. Photomicrographs were acquired using TappingModeTM AFM (TM-AFM) under ambient conditions. With a TM-AFM, the tip is driven at a known amplitude and frequency of oscillation which is typically near the cantilever resonance. The oscillatory motion is reduced as the tip is brought closer to the surface. The changes in the amplitude allow the AFM to track the surface, providing topographical information. A single crystal silicon NanoprobeTM with a spring constant of *ca* 17–43 N/m and resonance frequencies in the 262–359 kHz range was used to examine the xerogel film surfaces. TappingModeTM AFM images were acquired at a 1- μ m and 5- μ m scan size with the z-scale set to 100-nm.

Phase mode AFM imaging can distinguish surface features that are related to surface composition differences. Phase shifts are registered as bright and dark regions in the phase AFM image. For the phase mode images of this study, brighter regions indicate stiffer material whereas darker regions indicate a softer material.

Comprehensive contact angle analysis

The xerogel films were stored in air prior to characterization. Comprehensive contact angle analyses were performed in air (Zisman 1964; Baier and Meyer 1992). The approximate sampling depth of the contact angle technique is 5 Å. Up to 13 different diagnostic liquids were utilized for the analysis of each sample, viz. water, glycerol, formamide, thiodiglycol, methylene iodide, 1-bromonaphthalene, 1-methylnaphthalene, dicyclohexyl, n-hexadecane, n-tridecane, *n*-decane, *n*-octane, and *n*-heptane. The liquid/vapor surface tensions of these liquids were determined directly; reference values for the liquid/vapor surface tensions are not used. The technique of "advanced angle" analysis was used, wherein a sessile drop of liquid (8–15 μ l depending on the viscosity of the liquid) is placed on the sample surface and the angle of contact (θ) between the liquid and the solid is measured with a contact angle goniometer [Rame-Hart, Model NRL 100]; both sides of the droplet profile are measured. Another droplet of the same fluid is placed on top of the first droplet (the fluid is advanced across the surface), and the measurements are repeated. If the contact angles for the first droplet are $<20^{\circ}$, no further measurements are taken for that liquid on the sample; fluids having contact angles of $<20^{\circ}$ use a relatively large amount of the limited sample surface area. Zisman plots were constructed by plotting the cosine of the average angle measured for each liquid against the liquid/vapor surface tension of the diagnostic liquid. A linear least squares analysis is performed to determine the sample's critical surface tension (γ_C) at the cos $\theta = 4$ axis. In cases of large data scatter (non linearity), the data for the spreading liquid $(\theta = 0)$ with the greatest liquid/vapor surface tension and for those liquids closest to, but greater than, in surface tension to the first spreading liquid are used to determine γ_C . The data were also treated as described by Owens and Wendt (1969), Kaelbe (1970), and Nyilas et al. (1977) to give the surface free energy ($\gamma_{\rm S}$),

as well as its polar (γ_P) and dispersion (γ_D) components (Baier and Meyer 1992), after the xerogel films were aged in air or soaked in deionized water for 48 h and then air-dried for 1 h.

Static water contact angles (θ_{Ws}) were measured by the sessile drop technique where the angle between a 15- μ l drop of water and the xerogel surface was measured with a contact angle goniometer [Rame-Hart, Model NRL 100]; both sides of the droplet profile were measured.

Biofouling assays with barnacles

Barnacle cypris larvae were obtained from Duke University Marine Lab. Glass standards were acid washed in 10% HCl for 2 h, rinsed well with deionized water, and dried completely prior to cyprid settlement. Silastic[®] T2 (T2) coated slides (Feinberg et al. 2003) were included in the assays to provide a standard FR coating.

Cyprid settlement assays

Approximately 10 ml of seawater were added to each xerogel-coated Petri dish. This volume covered the bottom of the dish and allowed the cyprids free range of movement across the surface. A 400- μ l drop of seawater containing between 30 and 60 2–4-day-old barnacle cypris larvae was then added to each of the dishes. After 48 h the percentage of cyprids that had settled in each dish was counted. The average percentage settlement for each of the experimental coatings was compared to the controls. Glass and T2 coated dishes were used as standard settlement substrata.

Barnacle removal assays

A 400- μ l drop of seawater containing between 20 and 40 2–4-day-old cypris larvae was placed on the surface of the xerogel film-coated glass microscope slides. The surfaces with larvae were placed in a constant temperature incubator at 25°C on a 12 h:12 h light:dark cycle and the larvae were allowed to settle for 48 h. Newly metamorphosed juveniles on their respective coatings were transferred to growth chambers where they were fed the unicellular green alga Dunaliella tertiolecta and the diatom Skeletonema costatum for 2 weeks, and then a mixture of D. tertiolecta, S. costatum, and naupliar larvae of Artemia sp. for an additional week. Juveniles were then transferred to a 16-1 aquarium tank in an automated rack system with temperature, salinity, and pH monitors and programmed for a 10% daily water change. Barnacles in the tank were fed a 500-ml flask

of *Artemia* sp. three times a week for 4–6 weeks, which is the time it took the juvenile barnacles to reach a basal plate diameter of 3–5 mm, the minimum size necessary to conduct force gauge tests according to ASTM D 5618.

The procedures for critical removal stress were followed from ASTM D 5618 with the following modifications: (i) the force measuring device was operated by a motorized stand, ensuring a constant application of force during dislodgement, and (ii) barnacle dislodgement studies from coatings were performed under water. The apparatus consists of an IMADA ZP-11 digital force gauge mounted on an IMADA SV-5 motorized stand. The slides are clamped into a custom-built Plexiglas chamber that allowed their complete submersion during dislodgement tests.

Juvenile barnacles were selected for testing based on healthy appearance and minimum size requirements. Only barnacles positioned at least 5 mm from the edges of the slide were tested. Other barnacles in close proximity to the test subject were removed if they could potentially interfere with measurements. Prior to removal of barnacles each basal plate was photo-graphed using a CanonTM EOS 10D camera attached to an OlympusTM SZX12 dissecting microscope and images were later used to calculate basal plate areas using NIH's ImageJ software. After photographs were taken, the slide was clamped into the Plexiglas chamber. The force gauge mounted on the motorized stand was used to apply a shear force to the base of the barnacles at a rate of $\sim 4.5 \text{ N s}^{-1}$ until the organism was detached. Force was applied parallel to the film surface. The force required for detachment was noted and observations were made as to the mode of failure. If any portion of the base of the organism was left attached to the substratum, the test was deemed void for removal. The surfaces were examined visually for damage to the xerogel film caused by barnacle removal and by stereomicroscope if there were any ambiguity. The critical removal stress was calculated by dividing the force (F, Newtons) required to remove the test subject by the area of attachment (A, mm²). For barnacles where a portion of the base of the organism was left attached to the substratum, the remaining basal plate was photographed and the area was calculated as described above and used to calculate the exact fraction remaining after testing (fraction BPR).

Biofouling assays with Ulva

Coatings applied to glass slides were equilibrated in circulating deionized water for 48 h prior to the start of assays with algae. One hour prior to the assay, the slides were transferred to artificial seawater (ASW). Silastic[®] T2-coated slides were included in the assays to provide a standard FR coating.

Settlement of zoospores of Ulva

Fronds of Ulva linza were collected from Llantwit Major, Wales (51840'N; 3848'W) and a spore suspension of 1.0×10^6 spores ml⁻¹ was prepared by the method of Callow et al. (1997). Three replicate slides of each treatment were placed in individual wells of "quadriperm" polystyrene culture dishes (Greiner) and 10 ml of spore suspension were added. Dishes were incubated in the dark for 1 h at $\sim 20^{\circ}$ C. After incubation, the slides were gently washed in ASW to remove unattached (swimming) spores. Slides were fixed in 2.5% glutaraldehyde. The density of spores attached to the surfaces was counted using an image analysis system attached to a fluorescence microscope. Spores were visualized by autofluorescence of chlorophyll. Counts were made for thirty fields of view (each 0.17 mm^2), 1 mm apart over the central region of each slide, using image analysis software (Axiovision 4.8.1, Carl Zeiss imaging systems) attached to a Zeiss epifluorescence microscope (Callow et al. 2002). Spore settlement data are expressed as the mean number of spores adhered per mm² with 95% confidence limits (n = 40).

Adhesion strength of sporelings of Ulva

Spores were allowed to settle as described above. After washing away unattached spores, spores that had attached to the test surfaces were cultured in dishes containing supplemented seawater medium that was changed every 2 days (Starr and Zeikus 1987). The dishes were placed in an illuminated incubator (75 mW $m^{-2} s^{-1}$ incident irradiation) for 7 days during which time the spores germinated and developed into sporelings.

The biomass produced was quantified by measuring the fluorescence of chlorophyll in a Tecan fluorescence plate reader (excitation = 430 nm, emission = 670 nm) (Finlay et al. 2008a). Fluorescence was measured as relative fluorescence units (RFU) and was directly proportional to the quantity of biomass present. The RFU value for each slide was the mean of 70 point fluorescence readings taken from the central region (middle third of the slide over a 1 in \times 1 in region).

The strength of adhesion of the sporelings was determined by exposing the slides to a range of impact pressures from an automated water jet, which traversed the central region (middle third of the slide over a 1 in \times 1 in region) of each slide (Finlay et al. 2002). One replicate slide of each coating was exposed to one

of five impact pressures. Pressures were selected to provide the widest range of biomass removal possible. The biomass that remained in the sprayed area after exposure to the water jet was quantified as described above. The percentage removal of sporelings was determined by comparison of the biomass (RFU) before exposure with that remaining attached to the coatings after exposure to the water jet. The critical impact pressure to remove 50% of the biomass (CP₅₀) was determined from plots of percentage removal *vs* water impact pressure (Finlay et al. 2008a).

Results

Xerogel surfaces

A series of xerogel surfaces containing C18, TDF, C8 and TEOS were prepared from sols with the following mole-% ratios: 1:1:48:50, 1:4:45:50, 1:9:40:50, 1:14:35:50, 1:19:30:50 and 1:24:25:50 C18/TDF/C8/ TEOS, respectively. A 1:49:50 C18/TDF/TEOS xerogel surface (C18/TDF/TEOS xerogel in the remainder of the manuscript) was also prepared and a 50:50 C8/ TEOS xerogel surface (C8/TEOS xerogel in the remainder of the manuscript) was prepared as a xerogel control. The xerogel films prepared by spin coating were 1–2 μ m thick as measured by profilometry. All of the xerogel films of this study were optically transparent.

The xerogel surfaces were aged in air at ambient temperature for 7 days and were then examined by comprehensive advanced contact angle analyses to give values of the critical surface tension (γ_C) (Zisman 1964; Baier and Meyer 1992) and the surface free energy (γ_S) (Owens and Wendt 1969, Table 1). The static water contact angles, θ_{Ws} , were measured for all xerogel surfaces described in this study and are compiled in Table 1. For the TDF-containing xerogels, values of $\gamma_{\rm C}$ varied between 11.5 and 19.8 mN m⁻¹, values of $\gamma_{\rm S}$ varied between 16.1 and 21.8 mN m⁻¹ and values of $\theta_{\rm Ws}$ varied between 97.0° and 110.3°.

To evaluate the impact of water on surface properties, values of θ_{Ws} and γ_S were measured before and after the xerogel surfaces were immersed in deionized water for 48 h and air-dried for 1 h. The values of θ_{Ws} and γ_S , pre- and post-immersion in deionized water, are compared graphically in Figure 1. In pair-wise comparisons (Student *t*-test), values of γ_S pre-and post-immersion in water are essentially unchanged with no significant differences (p > 0.09) with the exception of the 1:19:30:50 C18/TDF/C8/TEOS xerogel where the increase in γ_S upon immersion in water was significant (p < 0.01).

The 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogels were examined by AFM prior to immersion in water and after 24 h immersion in deionized water. Immersed surfaces were air-dried for 1 h prior to imaging in air. Figure 2 shows representative images of the 1:4:45:50 C18/TDF/C8/TEOS xerogel prior to immersion (panels a–c) and post-immersion in deionized water (panels d–f). The phase images of the pre-immersion samples (panels b and c) clearly show inhomogeneities across the surface, which may be linked to phase segregation. After immersion in water, the features of inhomogeneity are smaller and are more evenly distributed across the surface.

Values of the root-mean-square roughness ($R_{\rm rms}$) for the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogel surfaces pre- (1.87 ± 0.20 and 2.31 ± 0.21 nm, respectively, where error limits are ± one standard deviation [SD]) and post-immersion (0.93 ± 0.05 and 0.95 ± 0.03 nm, respectively) in deionized water were calculated on six 5- μ m × 5- μ m images for each sample, where $R_{\rm rms}$ is defined as the

Table 1. Static water contact angles (θ_{Ws}), critical surface tensions (γ_C) and surface energies (γ_S) for the xerogel surfaces of this study and glass, T2 and C8/TEOS standards.

Sample	$ heta_{\mathbf{Ws}}{}^{a},^{\circ}$	$\gamma_{\rm C}^{\ b}$, mN m ⁻¹	$\gamma_{\rm S}^{\ c}$, mN m ⁻¹
Glass	21 ± 1	_	_
T2	109^{d}	23.0 ± 0.4^{e}	23.0 ± 0.4^{d}
50:50 C8/TEOS	100^{f}	21.3 ± 0.1^{f}	27.1 ± 0.3^{f}
1:1:48:50 C18/TDF/C8/TEOS	110.3 ± 0.7	_	21.8 ± 1.6
1:4:45:50 C18/TDF/C8/TEOS	102.4 ± 0.8	19.3 ± 1.4	21.8 ± 2.8
1:9:40:50 C18/TDF/C8/TEOS	100.8 ± 1.6	19.8 ± 0.5	20.1 ± 1.4
1:14:35:50 C18/TDF/C8/TEOS	98.9 ± 1.6	18.8 ± 0.2	17.6 ± 0.5
1:19:30:50 C18/TDF/C8/TEOS	100.7 ± 0.3	11.5 ± 2.3	17.2 ± 0.5
1:24:25:50 C18/TDF/C8/TEOS	100.8 ± 0.1	12.4 ± 0.5	16.1 ± 3.0
1:49:50 C18/TDF/TEOS	97.0 ± 1.1	_	17.3 ± 0.5

^{*a*}Mean of five independent measurements for coatings stored in air prior to measurement. \pm one SD. ^{*b*}Mean of two independent measurements for coatings stored in air for 7 days prior to measurement. ^{*c*}Mean of three independent measurements for coatings stored in air for 7 days prior to measurement. ^{*d*}From Tang et al. (2005). ^{*e*}From Feinberg et al. (2003). From Gunari et al. (2011).



Figure 1. Changes in (a) static water contact angle (θ_{Ws}) and (b) surface energy (γ_S) between xerogel samples air-dried for 7 days (black bars) and xerogels samples soaked for 48 h in deionized water (white bars). Error bars represent \pm one SD from the mean for three independent measurements preand post-immersion.

root mean square average of the topographic deviations (t) as shown in Equation (1):

$$R_{\rm rms} = \left\{ \sqrt{\left| \left(\sum_{i=1}^{N} \left(t_i - \overline{t} \right)^2 \right) \right|} \right\}$$
(1)

Values of $R_{\rm rms}$ pre- and post-immersion in deionized water as well as changes in the peak-to-valley heights are shown graphically in Figure 3. Immersion in water for both surfaces led to statistically significant decreased surface roughness in pair-wise comparisons (Student *t*-test, p < 0.0001 for both surfaces) and decreased peak-to-valley heights (p = 0.0002 and p < 0.0001 for the 1:4:45:50 and 1:14:35:50 C18/ TDF/C8/TEOS xerogel surfaces, respectively).

Samples of the 1:4:45:50 and 1:14:35:50 C18/TDF/ C8/TEOS xerogel on aluminum-coated glass slides were also examined by imaging reflectance IR microscopy. The sol-gel process produces xerogels with residual silanol functionality (3200–3700 cm⁻¹), which is uniformly distributed across the 1:4:45:50 and

1:14:35:50 C18/TDF/C8/TEOS xerogels (IR microscopy images not shown) as well as across the C8/ TEOS and 1:49:50 C18/C8/TEOS xerogel surfaces of earlier studies (Gunari et al. 2011). In contrast, IR microscopy images of the integrated C-F stretching region $(1223-1275 \text{ cm}^{-1})$ and the integrated C-H stretching region (2800–3000 cm^{-1}) show some segregation into higher C-F/lower C-H-containing features and lower C-F/higher C-H-containing features across the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogel surfaces. These features are illustrated in Figure 4 for the 1:14:35:50 C18/TDF/C8/TEOS xerogel prior to immersion (panels a and b) and post-immersion in deionized water for 24 h (panels d and e). A ratio of the two images (C-F/C-H), resulting in a single image in which black areas reflect regions with enhanced signal from fluorocarbon species or decreased signal from hydrocarbon species and white areas reflect regions with enhanced signal from hydrocarbon species or decreased signal from fluorocarbon species as shown in panel c and f of Figure 4. Enhanced fluorocarbon and hydrocarbon features on the $\sim 1 \,\mu$ m-scale are discernable pre- and post-immersion in water. It should be noted that these features are with respect to the "bulk" surface, ie the entire thickness, and are not necessarily an indication of chemical identity at the surface.

Settlement of cypris larvae and removal of juvenile barnacles of B. amphitrite

The settlement of 2–4-day-old barnacle cypris larvae that were placed on the xerogel coatings and the glass and T2 standard surfaces was compared (Figure 5). There was no significant difference in settlement between individual xerogel test coatings or between xerogel test coatings and glass or T2 standards (ANOVA, p = 0.233). The fraction of settled cyprids among the xerogel coatings was between 0.32 and 0.59.

The strength of attachment of juvenile barnacles to the seven TDF-containing xerogel surfaces, the C8/ TEOS xerogel and glass and T2 standards was measured via force-gauge measurements with forces applied in shear. All barnacles on both the C8/TEOS xerogel and the glass standard broke when force was applied to them in shear, and left a complete or partial basal plate attached to the surface. For the glass standard, the fraction of the barnacle basal plate remaining was 1.00, ie essentially all of the barnacle basal plate remained on the glass surface. For the C8/TEOS xerogel, the fraction of the barnacle basal plate remaining was 0.80 ± 0.04 . All of the TDF-containing xerogel surfaces as well as the T2 standard performed as FR surfaces as shown in Figure 6a. The 1:1:48:50 C18/TDF/C8/TEOS xerogel gave complete release of



Figure 2. AFM images of the 1:4:45:50 C18/TDF/C8/TEOS xerogel. Panels (a)–(c) are the surfaces prior to immersion in deionized water. Panels (d)–(f) are post-immersion for 24 h in deionized water and air-dried for 1 h. Panels (a) and (d) compare AFM height images (image size: $5 \ \mu m \times 5 \ \mu m$, Z-range: 100 nm). Panels (b) and (e) compare the subsequent phase images. Panels (c) and (f) compare the phase images acquired at a 1 $\mu m \times 1 \ \mu m$ scan size. All AFM images were acquired in air.

30% of the attached barnacles (6/20 barnacles removed completely) while the C18/TDF/TEOS xerogel gave complete release of 20% of attached barnacles (4/20 barnacles removed completely). The 1:4:45:50 and the 1:14:35:50 C18/TDF/C8/TEOS xerogels (fraction removed completely = \leftarrow 1.00 and 0.94, respectively) were comparable to the T2 standard (fraction removed completely = \leftarrow 93, Figure 2a). The 1:9:40:50, 1:19:30:50 and 1:24:25:50 C18/TDF/C8/ TEOS xerogels gave intermediate performance (fraction removed completely = \leftarrow 6.69–0.85).

There was a significant difference in critical removal stress (CRS) between test coatings (ANOVA p < 0.001). The value of CRS for the 1:1:48:50 C18/ TDF/C8/TEOS xerogel surface $(0.24 \pm 0.01 \text{ MPa},$ Figure 6b) was significantly higher in comparison to the other TDF-containing xerogel surfaces and the T2 standard (in pair-wise comparisons using the Student t-test). Values of CRS for the 1:4:45:50, 1:9:40:50, 1:14:35:50, 1:19:30:50 and 1:24:25:50 C18/TDF/C8/ TEOS xerogel surfaces and the C18/TDF/TEOS xerogel surface were 0.12 to 0.20 MPa. These values are not significantly different from the CRS for the T2 surface (0.14 \pm 0.01 MPa). The value of CRS for the 1:14:35:50 C18/TDF/C8/TEOS xerogel surface

(0.12 \pm 0.01 MPa) was significantly lower in comparison to CRS for the C18/TDF/TEOS xerogel surface (0.20 \pm 0.02 MPa).

Berglin et al. (2001) suggested that the remaining fraction of the basal plate left on a surface appeared to be a function of barnacle bioadhesive bond strength and that it could be used as a measure of the efficacy of FR coatings. For barnacles not completely removed, the percentage of the basal plate remaining (BPR) was calculated with digital image analysis. These results were combined with data for barnacles completely removed (fraction BPR = (0.0) and are shown in Figure 6c. The fraction of the BPR on the T2 standard was 0.02 + 0.01 (Figure 6c). In pair-wise comparisons, the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/ TEOS xerogel surfaces retained significantly less of the basal plate (p < 0.05) than the T2 standard, the 1:1:48:50 C18/TDF/C8/TEOS xerogel and the C18/ TDF/TEOS xerogel retained significantly more of the basal plate than the T2 standard and the other TDFcontaining xerogels (p < 0.02), while the glass standard and C8/TEOS xerogel control retained essentially all of the basal plate (fraction BPR = 4.00 and 0.80 ± 0.04 , respectively), which was significantly greater than all of the other surfaces (p < 0.0001).



Figure 3. Changes in surface topography for the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogels as measured by changes in (a) micro surface roughness and (b) AFM peak-to-valley distances pre-immersion (black bars) and post-immersion (white bars) for 24 h in deionized water and airdried for 1 h. Averages were calculated from measurements on six 5 μ m × 5 μ m images. Error bars represent one SD from the mean.

Settlement and removal of zoospores of Ulva

Settlement of zoospores, the growth of sporeling biomass and the impact pressure needed to remove 50% from the TDF-containing xerogel surfaces, the

C8/TEOS xerogel control, and the T2 standards were examined. Spore settlement densities on the C18/TDF/ C8/TEOS coatings and the C8/TEOS xerogel did not follow a trend in terms of composition of the C18/ TDF/C8/TEOS xerogels (Figure 7). One-way analysis of variance and Tukey tests indicated significant differences among the C8/TEOS control and TDFcontaining coatings (F_{7, 712} = 33.0 p < 0.05). Settlement densities on the 1:1:48:50 and 1:24:25:50 C18/ TDF/C8/TEOS xerogels were significantly lower in comparison to settlement on the C8/TEOS xerogel control or the other TDF-containing xerogels. Zoospore settlement densities on the 1:4:45:50 C18/TDF/ C8/TEOS xerogel and the C18/TDF/TEOS xerogel were not significantly different in comparison to those on the C8/TEOS xerogel control. Settlement densities were highest on the 1:4:45:50, 1:9:40:50, 1:14:35:50, and 1:19:30:50 C18/TDF/C8/TEOS xerogels, which are the mid-range of the TDF/C8 ratios, and were not significantly different from one another.

Strength of attachment of sporelings of Ulva

Sporelings grew well and after 7 days, a green covering was visible on all surfaces. The TDF-containing xerogels and the C8/TEOS control and glass and T2 standards were exposed to a range of water pressures (20-54 kPa) to determine the critical water pressure (CP₅₀) required to remove 50% of 7-day sporeling biomass (Finlay et al. 2008a). These values are shown graphically in Figure 8. Values of CP₅₀ for all of the C18/TDF/TDF/TEOS xerogels and the C8/TEOS xerogel fell in the range 23.5-36 kPa and are comparable to CP_{50} (23 kPa) for the T2 surface. The similarity of CP₅₀ for the TDF-containing xerogels and Cp₅₀ for the T2 surfaces was confirmed in a second experiment (see Supporting Information [Supplementary material is available via a multimedia link on the online article webpage]).

A value of CP_{50} could not be determined for the glass standard. At the highest pressure examined (54 kPa), the fraction of sporelings removed was < 0.2. In previous studies, CP_{50} for glass has been estimated at > 200 kPa (Finlay et al. 2008b) and, in the current study, would be estimated to be at least 100 kPa.

Discussion

Earlier studies of xerogel surfaces constructed from sol gels with short-chain (8 carbon atoms) organic functionality indicated that these materials had homogeneous surfaces both topographically and chemically (Tang et al. 2005; Bennett et al. 2010; Finlay et al. 2010). SEM studies of several xerogel surfaces indicate that these surfaces are uniform, uncracked, and



Figure 4. Imaging reflectance IR microscopy comparing 50 μ m × 50 μ m images of the fluorocarbon regions (C-F stretch, 1223–1275 cm⁻¹, panels a and d) and the hydrocarbon regions (C-H stretch, 2800–3000 cm⁻¹, panels b and e) of the 1:14:35:50 C18/TDF/C8/TEOS xerogel following air-drying for 7 days (panels a and b) or immersion in deionized water for 48 h (panels d and e). In panels (a) and (d), lighter regions represent higher C-F stretching intensity and darker regions, lower C-F stretching intensity. In panels (b) and (e), lighter regions represent higher C-H stretching intensity and darker regions, lower C-H stretching intensity. In the ratio images of panels (c) and (f) relative scales were set arbitrarily to enhance contrast, darker regions represent higher C-F/lower C-H intensity while lighter regions represent lower C-F/higher C-H intensity as indicated by the intensity bar. Images pre- and post-immersion are extracted from similar areas of each slide, but are not from identical coordinates. Intensity scales are identical pre- and post-immersion.

topographically smooth when dry (Bennett et al. 2010). AFM measurements on the same series of xerogels submerged in ASW show very low surface roughness (0.8 nm) and no phase segregation. Time-of-flight, secondary-ion mass spectrometry (ToF-SIMS) studies show that there is no phase segregation of fluorocarbon and hydrocarbon groups on the micrometer scale in a 25:25:50 trifluoropropyl-trimethoxysilane/C8/TEOS xerogel (Bennett et al. 2010).

More recent studies indicate that incorporating low levels (1–2 mole-%) of C18, a trialkoxysilane with a long-chain alkyl substituent, into the C8/TEOS xerogel produces topographical features on the nm- and μ mscale, ie pores *ca* 100–400 nm across and 2–7 nm deep (Gunari et al. 2011). Studies using the IR microscope with these same surfaces indicated some segregation of hydrocarbon content into micrometer-scale features (Gunari et al. 2011). These results indicate that chemical segregation in the bulk xerogel is possible and can lead to topographical features over multiple scales.

Polymers and block copolymers incorporating polyfluoroalkyl or perfluoroalkyl side chains display

some phase segregation in air and undergo surface reorganization upon exposure to water (Gudipati et al. 2004; Koberstein 2004; Makal et al. 2007; Martinelli et al. 2008). Many of the morphological changes are presumed to be driven by the presence of polyethylene glycol side chains in some of these systems and surface roughness increases upon exposure to water.

The C18- and TDF-containing xerogel coatings of this study showed decreased surface roughness upon exposure to water. Both AFM (Figure 2) and IR microscopy (Figure 4) showed non-homogeneous surfaces. Prior to immersion in water, topographic AFM images of the 1:4:45:50 and the 1:14:35:50 C18/ TDF/C8/TEOS xerogels showed spherical (ca 20-25 nm diameter) nanodomains that were segregated from the xerogel continuous phase (Figure 2a). Upon immersion in deionized water for 48 h, some surface reorganization was apparent: the spherical nanodomains become less apparent (Figure 2d) and, overall, there was a significant decrease in surface roughness as shown in Figure 3. AFM phase images showed a nonhomogeneous surface with nanodomains of ca 100-150 nm diameter prior to immersion in deionized



Figure 5. Settlement of barnacle cypris larvae on xerogel coatings applied to glass dishes, and glass and T2 standards. Each value is the mean from 3 replicate measurements. Error bars represent the SE of the mean.

water (Figure 2b) and much smaller domains after immersion (Figure 2e). The surface reorganization upon immersion in water (Figure 3) had minimal impact on measurable surface properties such as the surface free energy (γ_s) and the static water contact angle (θ_{Ws}), which were relatively unchanged pre- and post-immersion over the entire range of TDF concentrations (1 to 24 mole-%) in this study (Figure 1).

The nature of the cross-linking and functional group distribution in the xerogels differs from that of fluorinated block copolymers that undergo surface reorganization upon exposure to water (Gudipati et al. 2004; Koberstein 2004; Makal et al. 2007; Martinelli et al. 2008). Immersion in water did not change the relative intensity of the silanol bands in the surface regions shown in Figure 4 (data not shown) suggesting that further cross-linking of the surface is not responsible for the change.

The IR microscope showed some segregation of chemical functionality in the bulk xerogel on roughly the micrometer scale, which is the spatial resolution of the IR microscopy images (Figure 4). While the IR microscope does not give absolute hydrocarbon and fluorocarbon domains, micrometer-scale features characterized by either increased hydrocarbon content or increased fluorocarbon content are apparent in the "ratio" images of Figure 4 both pre- and postimmersion in water (panels c and f, respectively). Immersion in water appears to have little impact on the distribution of the larger micrometer-scale, bulk features, suggesting that surface reorganization is on the nanometer-scale within the regions of higher fluorocarbon and/or hydrocarbon content.



Figure 6. Fraction of juvenile barnacles removed completely *via* shear pressure (panel a), critical removal stress (CRS) in MPa for barnacles removed completely (panel b), and fraction of barnacle basal plate remaining (BPR) from those barnacles removed completely or incompletely (panel c). In panel (b), coatings that share a letter have values of CRS that are not significantly different from one another. Number of barnacles, n, removed completely in each group and total number of barnacles pushed given in panel (a). Error bars are the SE from the mean.

The experimental values of $\gamma_{\rm S}$ (Table 1) for the TDF-containing xerogels of this study are lower in comparison to values of $\gamma_{\rm S}$ for the C8/TEOS xerogel control surface and T2 standard surface and are also either below or at the low end of the 20–25 mN m⁻¹ range of the "Baier curve" where minimal bioadhesion has been reported (Baier et al. 1968; Baier 1984). Materials with lower values of $\gamma_{\rm S}$ have shown increased bioadhesion.



Figure 7. Settlement of zoospores of Ulva on 50:50 C8/ TEOS and TDF-containing xerogel coatings. Each value is the mean of 90 counts on each of 3 replicate slides. Error bars represent the 95% confidence limits. Coatings that share a letter have values for zoospore settlement that are not significantly different from one another.

Less than optimal performance might be expected for the lower surface energy materials as either AF or FR surfaces relative to surfaces with values of $\gamma_{\rm S}$ in the 20–25 mN m⁻¹ range of the "Baier curve" if surface energy alone were the sole determining factor. The T2 standard, for example, has $\gamma_{\rm S}$ of 23.0 \pm 0.4 mN m⁻¹ (Feinberg et al. 2003), which is in the middle of the Baier minimum. In particular, the 1:4:45:50 through 1:24:25:50 C18/TDF/C8/TEOS surfaces had values of $\gamma_{\rm C}$ in the range 11.5–19.8 mN m⁻¹ and values of $\gamma_{\rm S}$ in the range 16.1–21.8 mN m⁻¹ and gave release of 68– 100% of juvenile barnacles. In contrast, the 50:50 C8/ TEOS xerogel with $\gamma_{\rm C}$ of 21.3 mN m⁻¹ and $\gamma_{\rm S}$ of 27.1 mN m⁻¹ in the middle of the Baier minimum gave 0% release of juvenile barnacles.

Settlement studies of cypris larvae of the barnacle *B. amphitrite* showed that there were no significant differences between the TDF-containing xerogel test coatings and the C8/TEOS xerogel control surface or glass and T2 standards (Figure 5). The TDF-containing and C8/TEOS xerogels and the T2 surface are all hydrophobic surfaces ($\theta_{Ws} \ge 97^{\circ}$) and the range of surface energies, which are fairly similar among these coatings (~ 10 mN m⁻¹ range), had no significant impact on settlement.

Settlement studies of zoospores of *Ulva* indicated significant differences among the C8/TEOS and TDF-containing coatings, but these differences did not correlate with either θ_{Ws} or with γ_{S} . Settlement densities on the 1:1:48:50 and 1:24:25:50 C18/TDF/C8/TEOS xerogels were significantly lower in comparison to settlement on the C8/TEOS xerogel standard



Figure 8. Critical water pressure (CP_{50}) to remove 50% of sporelings of *Ulva* from the T2 standard and the C18/TDF/C8/TEOS and C18/TDF/TEOS xerogel coatings.

while settlement on the 1:4:45:50 C18/TDF/C8/TEOS xerogel and the C18/TDF/TEOS xerogel was not significantly different in comparison to settlement on the C8/TEOS xerogel standard. All four of these surfaces had values of $\gamma_{\rm S}$ (17.2–21.8 mN m⁻¹) well below that of the C8/TEOS xerogel (27.1 mN m⁻¹). In contrast, settlement densities were highest on the 1:4:45:50, 1:9:40:50, 1:14:35:50, and 1:19:30:50 C18/ TDF/C8/TEOS xerogels with values of $\gamma_{\rm S}$ in the same range. With the exception of the 1:1:48:50 C18/TDF/ C8/TEOS xerogel ($\theta_{Ws} = 410^{\circ}$), all of the other xerogel surfaces including the C8/TEOS xerogel had a value of $\theta_{\rm Ws}$ of ~ 100° (within experimental error). On these surfaces, settlement of zoospores does not appear to be correlated with either total surface energy or hydrophobicity.

The TDF-containing xerogel surfaces acted as FR surfaces with several comparable to the T2 standard with respect to release of juvenile barnacles and 7-day Ulva sporeling growth. The 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogel surfaces and T2 standard gave essentially complete release of juvenile barnacles (Figure 6). Values of the critical removal stress (CRS) were statistically identical among these three coatings (0.12–0.14 MPa). The remaining TDF-containing coatings also functioned as FR surfaces although not as effectively as the 1:4:45:50 and 1:14:35:50 C18/TDF/ C8/TEOS xerogel surfaces. In contrast, the C8/TEOS xerogel surface did not function as a FR surface, ie all barnacles broke before removal (Figure 6). Again, there is no direct correlation of individual coating performance with either $\gamma_{\rm S}$ or $\theta_{\rm Ws}$. Values of CP₅₀ for 7-day sporeling removal were comparable on all of the C18/TDF/C8/TEOS xerogel surfaces and were

described by a narrow range (23.5–36 kPa), which was comparable to the T2 standard as shown in Figure 8.

The data for 7-day sporeling removal taken with the performance of the TDF-containing xerogel surfaces for removal of juvenile barnacles suggest that the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogels perform similarly to the T2 standard as FR surfaces. The thinner, harder xerogel surfaces may release the macrofoulers *via* shear rather than by peeling as might be expected with T2 and related silicone elastomers (Brady and Singer 2000; Berglin et al. 2003; Kim et al. 2007; Ramsay et al. 2008).

The chemical segregation of the C18/TDF/C8/ TEOS xerogels of this study into nanometer- and micrometer-domains of higher fluorocarbon and hydrocarbon content likely contributes to the FR performance observed in these systems in addition to other surface properties. Nanotexture has previously been correlated with superhydrophobicity (Genzer and Efimenko 2006; Genzer and Marmur 2008) and improved AF/FR performance of coatings has been attributed to topography at the nanoscale (eg Beigbeder et al. 2008; Akesso et al. 2009; Grozea et al. 2009; Martinelli et al. 2009; Scardino and deNys 2011). However, these systems were presumed to be chemically homogeneous. Similarly, patterned surfaces with well-defined distances between pillars, channels and bioinspired designs such as SharkletTM have also been effective at minimizing fouling (Schumacher et al. 2007; Long et al. 2010; Magin et al. 2010). Again, these surfaces, while patterned, are chemically homogeneous. Recent data suggest that barnacle cyprids select textures to which they can adhere most strongly (Aldred et al. 2010). The hydrophobic nature of C18/TDF/C8/TEOS xerogel coatings and low surface energy likely contribute to their FR behavior, as well.

Xerogel surfaces can be fine-tuned to provide surfaces with different wettability and values of $\gamma_{\rm C}$ or $\gamma_{\rm S}$ (Tang et al. 2005; Bennett et al. 2010; Finlay et al. 2010; Gunari et al. 2011). The topography of the xerogel surfaces can also be fine-tuned by the incorporation of a long-chain alkyl component and varying amounts of the polyfluorinated TDF as shown by the xerogels of this study. The formulation and coating of these TDF-containing xerogel surfaces require no special attention or preparation (prepatterning). Depositing the xerogel by spin coating leads to self-segregation of hydrocarbon and fluorocarbon domains.

Overall, xerogel surfaces have high potential as FR or easy-clean materials with the 1:4:45:50 and 1:14:35:50 C18/TDF/C8/TEOS xerogels of this study being perhaps the most promising leads yet in xerogel surface chemistry. These coatings may be useful as AF/FR surfaces in applications where thicker coatings are

not optimal or practical. In particular, these coatings, as with other xerogel coatings, are optically transparent (Brinker and Scherer 1990; Avnir 1995; Ingersol and Bright 1997) and have applications as AF/FR coatings where optical transparency is important (marine sensors, underwater cameras, submersible solar panels).

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