A comparison between different fouling-release elastomer coatings containing surface-active polymers

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Surface-active polymers derived from styrene monomers containing siloxane (S), fluoroalkyl (F) and/or ethoxylated (E) side chains were blended with an elastomer matrix, either poly(dimethyl siloxane) (PDMS) or poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS), and spray-coated on top of PDMS or SEBS preformed films. By contact angle and X-ray photoelectron spectroscopy measurements, it was found that the surface-active polymer preferentially populated the outermost layers of the coating, despite its low content in the blend. However, the self-segregation process and the response to the external environment strongly depended on both the chemistry of the polymer and the type of matrix used for the blend. Additionally, mechanical testing showed that the elastic modulus of SEBS-based coatings was one order of magnitude higher than that of the corresponding PDMS-based coatings. The coatings were subjected to laboratory bioassays with the marine alga Ulva linza. PDMS-based coatings had superior fouling-release properties compared to the SEBS-based coatings.

Keywords: antifouling coatings; fouling-release coatings; amphiphilic polymers; films; surface tension; mechanical properties

Introduction

Biofouling is a worldwide problem that imposes a major economic burden on maritime industries (Schultz et al. 2011; Fitridge et al. 2012). Biocide-containing antifouling (AF) paints are effective in combating biofouling, but their use is becoming more restricted because of potential toxicity to the marine environment (Omee 2003; Yebra et al. 2004; Sonak et al. 2009; Thomas & Brooks 2010). Accordingly, in recent years a more environmentally friendly approach is being pursued by replacing traditional biocidal coatings with AF coatings that prevent the settlement (attachment) of the colonizing stages of fouling organisms and/or fouling-release (FR) coatings that reduce the adhesion of organisms so that they are removed by hydrodynamic forces such as those generated as a ship moves through the water (Lejars et al. 2012). From the many types of novel AF/FR coatings explored, recent advances include amphiphilic polymer systems (Krishnan et al. 2006; Dimitriou et al. 2011; Martinelli, Suffredini, et al. 2011; Wang, Pitet, et al. 2011), phase-segregated siloxane-polyurethane copolymers (Majumdar et al. 2007; Sommer et al. 2010), zwitterionic polymers (Jiang & Cao 2010) and polymer nanocomposites (Beigbeder et al. 2008; Carl et al. 2012). All such technologies typically exploit the interactions between the fouling organisms and the specific surface features at the nanoscale (Callow & Callow 2011). For example, it has been shown that the AF/FR performance of coatings containing amphiphilic copolymer systems depend on surface properties (Gudipati et al. 2004; Krishnan et al. 2006; Cho et al. 2011; Wang, Pitet, et al. 2011), which for efficient FR need to be combined with mechanical properties (modulus, friction, toughness) (Brady & Singer 2000; Kaffashi et al. 2012). The surfaces produced from amphiphilic copolymers, which simultaneously exhibit both hydrophilic and hydrophobic functionalities, have local nanoscale heterogeneities that deter the settlement of organisms and also minimize the intermolecular forces of interaction between biomolecules and substratum (Gudipati et al. 2005; Martinelli et al. 2008; Wang, Finlay, et al. 2011). Hence, the adhered organisms are released under appropriate shear stresses.

Two types of elastomers widely used to prepare experimental AF/FR coatings from amphiphilic polymers are poly(dimethyl siloxane) (PDMS) (Martinelli, Suffredini, et al. 2011; Martinelli, Sarvothaman, Galli, et al. 2012) and poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) (Krishnan et al. 2006; Martinelli et al. 2008; Weinman et al. 2009; Sundaram, Cho, Dimitriou, Weinman, et al. 2011; Sundaram, Cho, Dimitriou, Finlay, et al. 2011; Cho et al. 2011). Most current FR coatings are based on PDMS elastomers. In particular, those containing amphiphilic copolymers (eg Intersleek® 900, International Paint, Felling) have been shown to have

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superior AF and FR properties compared to first
generation products (eg Intersleek® 700) (Dobretsov &
Thomason 2011; Evariste et al. 2012; Sokolova et al.
2012). However, PDMS elastomers normally present low
tear strength, low adhesion to substrata and high cost.
No commercial SEBS-based coatings for FR applications
have been developed at this time. Nonetheless, SEBS
thermoplastic elastomers possess interesting properties,
including toughness, adhesion to different substrates,
ease of solubility and processability and low cost making
them possible alternatives to PDMS elastomers.
In a recent paper, Martinelli, Sarvothaman, Alderighi,
et al. (2012) reported on the surface properties of PDMS
networks containing copolymers carrying amphiphilic
side groups and showed their AF/FR release properties
on both laboratory scale and field trials (Martinelli, Sarvothaman, Galli, et al. 2012). The hydrodynamic
behaviour (Atlar et al. 2013) was also shown to be
superior compared to a hydraulically smooth reference
surface, thus making these coatings good candidates for
practical application. On the other hand, Weinman et al.
(2009) reported on the AF/FR performance of an
amphiphilic triblock copolymer deposited on SEBS
matrices with different elastic moduli. In particular, they
proved that reducing the elastic modulus of the
thermoplastic elastomer to a value similar to that of
commercial PDMS coatings (RTV11 and Intersleek®
700) enhanced the release of sporelings (young plants)
of the marine macroalga Ulva linza. However, as far as
the authors are aware, there are no papers that focus on
the wettability, surface and mechanical properties and FR
performance of coatings produced from the same polymers,
but dispersed in or deposited on different
elastomers, namely PDMS and SEBS.
To gain a deeper insight into the role of these factors
on the AF/FR properties, in this work novel copolymer
terpolymer samples characterized by different
philicity/phobicity were synthesized and blended in low
amounts with SEBS and PDMS and then deposited on top
of the corresponding elastomeric film. The amphiphilic
character was tuned by a combination of the hydrophobic
poly(dimethyl siloxane), hydrophilic poly(ethylene glycol)
and hydrophobic/lipophobic perfluoroalkyl styrhenic
constituents in the copolymer structure. The prepared coatings
were investigated by X-ray photoelectron spectroscopy
(XPS) and static contact angle measurements and their
mechanical properties were determined by tensile mea-
surements. The AF and FR performances were tested in
laboratory bioassays with the marine alga U. linza. AF
performance was determined by quantifying the number of
zoospores of U. linza that settled (attached) to the sur-
faces within a standard period of time. FR performance
was assessed by measuring the ease of removal of
sporelings of U. linza grown on the test coatings by
exposure to a calibrated shear stress.

**Experimental section**

**Materials**

4-Chloromethylstyrene, poly(ethylenglycol monomethyl
ether) \( (M_n = 550 \text{ g mol}^{-1}) \), 4-vinylbenzoic acid,
1H,1H,2H,2H-perfluorooctanol, bismuth neodecanoate,
\( N,N^\prime\)-dicyclohexylcarbodiimide (DCC), dimethylamino-
pyridine (DMAP) and trifluorotoluene (TFT) (Aldrich,
Milan) were used as received. 2,2′-Azobis-isobutyronitrile
(AIBN) (Fluka, Milan) was recrystallized from metha-
nol. Dichloromethane was refluxed over CaH$_2$ for 4 h
distilled under nitrogen. Tetrahydrofuran (THF) was
refluxed over Na/K alloy for 4 h and distilled under
nitrogen. Monocarbinol-terminated poly(dimethyl
siloxane) (PDMS-OH) \( (M_n = 1,000 \text{ g mol}^{-1}) \), bis(silanol)-
terminated poly(dimethyl siloxane) (HO-PDMS-OH)
\( (M_n = 26,000 \text{ g mol}^{-1}) \), poly(diethoxy siloxane) (ES40),
(3-glycidoxypropyl)trimethoxysilane (GPS) (ABCRL,
Karlsruhe) were used as received. Poly(styrene-b-(ethyl-
eneco-butylene)-b-styrene) (SEBS) triblock thermoplas-
tic elastomer (Kraton G1657 M, 13 wt% polystyrene)
and SEBS grafted with 1.4–2.0 wt % maleic anhydride
(SEBS-MA, Kraton FG1901X, 13 wt% polystyrene)
were kindly provided by Kraton Polymers (Belpre, OH).

**Synthesis of the monomer poly(dimethyl siloxane)
propoxymethyl 4-vinylbenzoate (S)**

For this process 1.210 g (8.17 mmol) of 4-vinylbenzoic
acid and 119 mg (0.96 mmol) of DMAP were dissolved
in 30 ml of anhydrous dichloromethane under a nitrogen
atmosphere. The mixture was cooled to 0°C and a solution
of 2.012 g (9.75 mmol) of DCC in 30 ml of
anhydrous dichloromethane was slowly added. The reaction mixture was stirred for 15 min at 0°C and 1 h at
room temperature. Then, a solution of 6.501 g (6.5
mmol) of PDMS-OH in 25 ml of anhydrous dichloromethane was slowly added. After stirring for 40
h the precipitate formed during the reaction was filtered off and the organic layer was washed with 10% Na$_2$CO$_3$,
5% HCl and water until neutrality and finally dried over
magnesium sulphate. The unreacted acid was removed
by repeated recrystallizations from n-hexane at ~20°C.
The solid was filtered off and the solvent was removed
under vacuum to give a colourless liquid (71% yield).

$^1$H-NMR (CDCl$_3$, δ in ppm): 0.1 (72H, SiCH$_3$), 0.5
(4H, SiCH$_2$), 0.5 (3H, CH$_3$CH$_2$), 1.3 (4H,
SiCH$_2$CH$_2$CH$_2$), 1.6 (2H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 3.5 (2H,
COOCH$_2$CH$_2$OH), 3.7 (2H, COOCH$_2$CH$_2$O), 4.5 (2H,
COOCH$_2$), 5.3–5.8 (2H, CH$_2$=), 6.7 (1H, CH=), 7.2–7.4
(4H, aromatic).
FT-IR (KBr pellet, ν in cm⁻¹): 2,961 (vCH aliphatic), 1,725 (v=O), 1,629–1,503 (vC=C aromatic and vinyl), 1,260 (vSiCH₃), 1,209–940 (vSiO and vCO), 801 (SiCH₃).

**Synthesis of the monomer 4-{(methoxypolyethylene glycol)ethyl(methyldimethyl)silyl}styrene (E)**

A mixture of 15.135 g (28 mmol) of poly(ethylene glycol monomethyl ether) and 55 ml of aqueous sodium hydroxide solution (50% w/w) was vigorously stirred at room temperature for 1 h, after which 0.751 g (2 mmol) of tetrabutylammonium hydrogen sulphate (TBAHS) in hydroxide solution (50% w/w) was added. Then, 4.603 g (30 mmol) of 4-chloromethylstyrene in 10 ml of dichloromethane was added to the suspension and the reaction mixture was stirred for 15 h at 40°C. The organic layer was separated, washed several times with 5% HCl and water until neutrality and dried over sodium sulphate. The solvent was removed under vacuum and the crude product was purified by double elution on silica gel (230–400 mesh) using methanol/dichloromethane (3/97 v/v) as an eluent (45% yield).

1H-NMR (CDCl₃, δ in ppm): 3.4 (3H, OCH₃), 3.5–3.8 (44H, OCH₂CH₂), 4.5 (2H, PhCH₂O), 5.2–5.8 (2H, CH₂=), 6.7 (1H, CH=), 7.2–7.4 (4H, aromatic).

FT-IR (KBr pellet, ν in cm⁻¹): 3,085 (νCH aromatic), 2,870 (νCH aliphatic), 1,629–1,458 (νC=C aromatic and vinyl), 1,107 (νCO).

**Synthesis of the monomer 4-{(2′-perfluorohexylethoxy)methyl}styrene (F)**

The monomer F was prepared according to a procedure in the literature (Hopken & Möller 1992). The crude product was purified by double elution on silica gel (230–400 mesh) with hexane/ethyl acetate (30/1 v/v) as an eluent (52% yield).

1H-NMR (CDCl₃, δ in ppm): 2.4 (2H, CH₂CF₂), 3.8 (2H, OCH₂), 4.6 (2H, PhCH₂O), 5.3–5.8 (2H, CH₂=), 6.7 (1H, CH=), 7.3–7.5 (4H, aromatic).

FT-IR (KBr pellet, ν in cm⁻¹): 3,090–3,010 (νCH aromatic), 2,877 (νCH aliphatic), 1,631–1,426 (νC=C aromatic and vinyl), 1,240–1,018 (νCO and CF), 652 (νCF₂).

**General procedure for the preparation of the copolymers p(S-F)x/y**

In a typical preparation, monomers S (1.194 g, 1.06 mmol) and F (0.081 g, 0.12 mmol), AIBN (14 mg) and THF (5 ml) were introduced into a Pyrex vial. The solution was outgassed by five freeze-pump-thaw cycles. The polymerization reaction was allowed to proceed under stirring at 65°C for 65 h. The crude product was purified by double elution on silica gel (230–400 mesh) using methanol/dichloromethane (3/97 v/v) as an eluent (45% yield).

1H-NMR (CDCl₃, δ in ppm): 0.1 (62.64H, SiCH₃), 0.5 (3.48H, SiCH₂), 0.7–2.2 (10.83H, CH₂–CH₂Si, SiCH₂–CH₂–CH₂Si, PhCH₂), 3.2–4.0 (9.59H, CO–OCH₂–CH₂–OCH₂, OCH₂–CH₂–OCH₂), 4.4 (2.00H, CO–OCH₂, PhCH₂O), 6.1–8.1 (4.00H, aromatic).

FT-IR (KBr pellet, ν in cm⁻¹): 2,996 (νCH aliphatic), 1,722 (ν=C=O), 1,647–1,482 (ν=C=C aromatic), 1,261 (νSiCH₃), 1,210–939 (νCO, νCF, νSiO), 799 (SiCH₃).

A series of p(S-F)x/y copolymers was prepared with varying content y of F co-units (y = 11–82 mol%) by changing the feed ratio of the two co-monomers.

**General procedure for the preparation of the terpolymers p(S-F-E)x/y/z**

In a typical preparation, monomers S (1.194 g, 1.06 mmol), F (0.081 g, 0.12 mmol) and E (0.081 g, 0.12 mmol), AIBN (14 mg) and THF (5 ml) were introduced into a Pyrex vial. The solution was outgassed by five freeze-pump-thaw cycles. The polymerization reaction was allowed to proceed under stirring at 65°C for 65 h. The crude product was purified by several extractions with methanol (yield 79%). The copolymer contained 13 mol% E co-units and was named p(S-E)87/13 (Mn = 18,000 g mol⁻¹, Mw/Mn = 1.47).

1H-NMR (CDCl₃, δ in ppm): 0.1 (62.64H, SiCH₃), 0.5 (3.48H, SiCH₂), 0.7–2.2 (10.83H, CH₂–CH₂Si, SiCH₂–CH₂–CH₂Si, PhCH₂), 3.2–4.0 (9.59H, CO–OCH₂–CH₂–OCH₂, OCH₂–CH₂–OCH₂), 4.4 (2.00H, CO–OCH₂, PhCH₂O), 6.1–8.1 (4.00H, aromatic).

FT-IR (KBr pellet, ν in cm⁻¹): 2,996 (νCH aliphatic), 1,722 (ν=C=O), 1,647–1,482 (ν=C=C aromatic), 1,261 (νSiCH₃), 1,210–939 (νCO, νSiO), 799 (SiCH₃).

A series of p(S-F-E)x/y/z copolymers was prepared with varying content z of E co-units (z = 13–43 mol%) by changing the feed ratio of the two co-monomers.
and was named p(S-F-E)56/18/26 ($M_n = 21,000 \text{ g mol}^{-1}$, $M_w/M_n = 1.57$).

$^1$H-NMR (CDCl$_3$, $\delta$ in ppm): 0.1 (40.32H, SiCH$_3$), 0.5 (2.24H, SiCH$_2$), 0.7–2.2 (8.04H, CH$_2$CH$_2$Si, SiCH$_2$CH$_2$CH$_2$CH$_3$, PhCHCH$_2$), 2.4 (0.36H, CH$_2$CF$_2$), 3.3–4.0 (14.82H, COOCH$_2$CH$_2$OH, PhCH$_2$OCH$_2$. OCH$_2$CH$_2$. OCH$_2$), 4.1–4.6 (2.00H, COOCH$_2$. PhCH$_2$O), 6.0–8.0 (4.00H, aromatic).

$^{19}$F-NMR (CDCl$_3$/CF$_3$COOH, $\delta$ in ppm): –5 (3F, CF$_3$), –38 (2F, CH$_2$CF$_2$), from –46 to –49 (6F, CF$_2$), –51 (2F, CF$_2$CF$_3$).

FT-IR (KBr pellet, $\nu$ in cm$^{-1}$): 2,962 ($\nu$CH aliphatic), 1,720 ($\nu$C=O), 1,652–1,487 ($\nu$C=C aromatic), 1,261 ($\nu$SiCH$_3$), 1,211–940 ($\nu$CO, $\nu$SiO, $\nu$CF), 800 (SiCH$_3$).

A series of p(S-F-E)x/y/z terpolymers were prepared with varying contents $y$ of F and $z$ of E co-units, respectively ($y = 18$–46 mol%, $z = 17$–30 mol%), by changing the feed ratio of the three co-monomers.

**Preparation of coatings**

Copolymers p(S-F)83/17 and p(S-E)87/13 and terpolymer p(S-F-E)56/18/26 were used as surface-active ingredients in either PDMS or SEBS to prepare two-layer coatings (Figure 1).

**PDMS-based coatings**

Glass slides ($76 \times 26 \text{ mm}^2$) were cleaned with acetone and dried in an oven for 30 min. Then they were kept in a piranha solution (H$_2$SO$_4$/H$_2$O$_2$ = 7/3 v/v) at 80°C for 2 h, washed with water followed by acetone and dried in an oven for 30 min. They were then kept overnight in a 2% (wt/v) solution of GPS in 95% ethanol (pH ~5 by acetic acid), rinsed with ethanol and heated at 110°C under vacuum. A bottom layer was formed by casting a 12% (wt/v) toluene solution of SEBS-MA/SEBS (56/44 wt/wt) onto glass slides. Then, the films were dried for 24 h and cured at 120°C for 12 h under vacuum. A top layer was formed by spray-coating a 3% (wt/v) toluene solution of SEBS blended with copolymer (7 wt% with respect to SEBS). The coatings were dried in air and annealed at 120°C for 12 h (overall thickness 150–200 µm).

**SEBS-based coatings**

Glass slides ($76 \times 26 \text{ mm}^2$) were cleaned with acetone and dried in an oven for 30 min. Then they were kept in a piranha solution (H$_2$SO$_4$/H$_2$O$_2$ = 7/3 v/v) at 80°C for 2 h, washed with water followed by acetone and dried in an oven for 30 min. They were then kept overnight in a 2% (wt/v) solution of GPS in 95% ethanol (pH ~5 by acetic acid), rinsed with ethanol and heated at 110°C under vacuum. A bottom layer was formed by casting a 12% (wt/v) toluene solution of SEBS-MA/SEBS (56/44 wt/wt) onto glass slides. Then, the films were dried for 24 h and cured at 120°C for 12 h under vacuum. A top layer was formed by spray-coating a 3% (wt/v) toluene solution of SEBS blended with copolymer (7 wt% with respect to SEBS). The coatings were dried in air and annealed at 120°C for 12 h (overall thickness 150–200 µm).

**Characterization**

$^1$H-NMR and $^{19}$F-NMR spectra were recorded with a Varian Gemini VRX300 spectrometer for CDCl$_3$ and CDCl$_3$/CF$_3$COOH solutions, respectively. Gel permeation chromatography (GPC) analyses was carried out using a Jasco PU–1,580 liquid chromatograph having two PL gel 5µm mixed-D columns, with a Jasco 830-RI refractive index detector. CHCl$_3$ was used as an eluent with a flow rate of 1 ml min$^{-1}$ and polystyrene standards were used for calibration.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC 30 instrument. Samples of 10–25 mg were used with 10°C min$^{-1}$ heating and cooling rates. Nitrogen was used as the purge gas at a flow rate of 30 ml min$^{-1}$. Temperature and energy calibrations were carried out using standard samples of tin, indium and zinc. The glass transition temperature ($T_g$) was taken as the inflection temperature in the second heating cycle.

![Figure 1](http://example.com/image1.png)  
**Figure 1.** Schematic representation of the PDMS- and SEBS-based two-layer coatings. Note: The PDMS-based coatings are composed of an additional layer (thickness ca. 2 µm) that is spray-coated onto glass and has the same composition as the PDMS layer.
Contact angles were measured by the sessile drop method with a FTA200 Camtel goniometer, using water \((\theta_w)\) (J. T. Baker, Center Valley PA, HPLC grade) and \(n\)-hexadecane \((\theta_h)\) (Aldrich product of the highest purity available) as wetting liquids. The measured values of \(\theta_w\) and \(\theta_h\) were used to extract the surface tension \((\gamma_s)\) of the polymer films according to the so-called Owens–Wendt–Kaelble approach (Owens & Wendt 1969; Kaelble 1970). In this approach the solid surface tension:

\[
\gamma_s = \gamma_s^d + \gamma_s^p
\]

yields:

\[
\gamma_L(1 + \cos \theta) = 2 \left( \frac{\gamma_s^d}{\cos \theta} + \frac{\gamma_s^p}{\sin \theta} \right)^{1/2}
\]

where \(\gamma_s^d\) and \(\gamma_s^p\) are the unknown dispersion and polar components of surface tension of the solid film, respectively.

Angle-resolved XPS spectra were recorded by using a Perkin-Elmer PHI 560 spectrometer with a standard Al-Kα source (1486.6 eV) operating at 350 W. The working pressure was less than 10\(^{-9}\) Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f\(_{7/2}\) line to be 84.0 eV with respect to the Fermi level. Extended (survey) spectra were collected in the range of 0–1350 eV (187.85 eV pass energy, 0.4 eV step, 0.05 s step\(^{-1}\)). Detailed spectra were recorded for the following regions: Si (2p), C (1s), O (1s) and F (1s) (11.75 eV step, 0.1 eV step, 0.1 eV s step\(^{-1}\)). The spectra were recorded at the two photoemission angles \(\phi\) (between the surface normal and the path taken by the electrons to the detector) of 70° and 20°, corresponding to sampling depths, \(d = d_0 \cos \phi\), where \(d_0\) is the maximum information depth \((d_0 \approx 10\) nm for the C 1s line) of \(\approx 3\) nm and \(\approx 8\) nm, respectively. The standard deviation (SD) in the BE values of the XPS line was 0.10 eV. The atomic percentage, after a Shirley type background subtraction (Shirley 1972), was evaluated using the PHI Vision 4 image analysis system attached to a Zeiss microscope (20 × objective; excitation 546 nm, emission 590 nm). The reported data are the average of 90 counts, 30 counts from each of the three replicate slides (each 0.15 mm\(^2\)). The resulting error bars show 95% confidence limits.

The six remaining slides of each sample were used to cultivate sporelings (young plants) of \textit{U. linza}. Ten millilitres of nutrient-enriched ASW (Starr & Zeikus 1987) were added to each compartment of the Quadriperm dishes, which were incubated at 18°C for 7 days with a 16 h:8 h light:dark cycle and an irradiance of 40 \(\mu\)mol m\(^{-2}\) s\(^{-1}\). The biomass of sporelings was determined in situ by measuring the fluorescence of the chlorophyll contained within the cells with a fluorescence plate reader (Tecan Genios Plus, Switzerland). The biomass was quantified in terms of relative fluorescence units (RFU) (Mieszkin et al. 2012).

The strength of attachment of sporelings was determined using a calibrated flow channel (Schultz et al. 2000, 2003) in which the slides were exposed to a wall shear stress of 52 Pa. The percentage removal was calculated from readings taken before and after exposure to flow, with 95% confidence limits calculated from arc-sine-transformed data. Differences between surfaces were tested using one-way ANOVA followed by Tukey’s test for pairwise comparisons as described in Mieszkin et al. (2012).

**Results**

**Synthesis of the polymers**

A novel styrene monomer carrying a hydrophobic poly(dimethyl siloxane) chain (S) was prepared by the esteri-
the same way to that of F (Figure 2).

Monomer S was alternatively polymerized with monomers F and E to produce two sets of copolymers with mixed side chains named as p(S-F)x/y and p(S-E)x/z, with different mole percentages (x, y and z) of each repeating co-unit (Figure 3). Moreover, in order to combine the properties of the hydrophobic/lipophobic monomer F with those of the hydrophilic monomer E, terpolymers were also prepared, named p(S-F-E)x/y/z, where x, y and z are the mole percentages of the three components, respectively (Figure 3). The formation of copolymers and terpolymers was confirmed by $^{1}$H-NMR, $^{19}$F-NMR and FT-IR spectroscopies and GPC analyses. Their chemical composition was evaluated from the integrated areas of the $^{1}$H-NMR signals at 0.5 ppm (SiCH$_2$ of S), 2.4 ppm (CH$_2$CF$_2$ of F) and 4.1–4.6 ppm (COOCH$_2$ of S and PhCH$_2$O of F and E). Full characterization data of the polymers prepared are given in the Supplementary Information [Supplementary material is available via a multimedia link on the online article webpage].

DSC analyses revealed that each set of polymers displayed a thermal behaviour that depended on both the chemistry and composition of the polymer. All the
copolymers p(S-F)x/y were amorphous and showed a glass transition temperature \( (T_g) \) at around \(-125^\circ C\), which correlated well with that of the siloxane homopolymer \( (T_g = -123^\circ C) \). On the other hand, a \( T_g \) attributable to the fluorinated co-units was detected only for the copolymer p(S-F)18/82 \( (T_g = 12^\circ C) \), richer in fluorine content. Similarly, the copolymers p(S-E)x/y showed a \( T_g \) at \(-124^\circ C\) due to the siloxane moieties, whereas a \( T_g \) associated with the ethoxylated component \( (T_g \sim -65^\circ C) \) was detected when the percentage of E was higher than 13 mol%.

Out of the different polymers prepared, copolymers p(S-F)83/17 and p(S-E)87/13 and terpolymer p(S-F-E)56/18/26 were selected as surface-active, amorphous polymers for film preparation since they contained comparable contents of F and E co-units.

### Preparation of coatings

SEBS- and PDMS-based coatings were prepared according to procedures reported in the literature (Martinelli et al. 2008; Pretti et al. 2013). In both types of coatings, a thin layer (~2 µm) of the surface-active polymer blended with the matrix (PDMS or SEBS at 93 wt%) was spray-coated on a thicker bottom layer of the matrix itself (150–200 µm). According to this procedure, the surface-active polymer was physically dispersed within the matrix and its migration to the surface was facilitated by annealing the test slides at 120°C for 12 h. The coatings appeared homogeneous and transparent with no macrophase separation detected by optical microscopy or atomic force microscope analyses. In the PDMS-based coatings the polymer was incorporated into a kind of semi-interpenetrating cross-linked PDMS network. This also avoided polymer leaching in water (Marabotti et al. 2009). Moreover, delamination of the coating during underwater evaluations was prevented by firm anchorage of the polymer coating to the glass surface that had been previously modified by deposition of a thin layer (~2 µm) of cross-linked PDMS or functionalization with reactive glycidyl groups for covalent bonding to the maleic anhydride residues of SEBS matrix. SEBS and SEBS-MA elastomers were chosen with a low content of polystyrene (13 wt%) in order to obtain a lowest elastic modulus matrix.

### Mechanical properties of the coatings

Stress (\( \sigma \))–strain (\( \varepsilon \)) mechanical tests were performed to evaluate the tensile properties of the coatings. SEBS, PDMS and their two-layer coatings containing 7 wt% p(S-E)87/13 in the top layer were investigated. Typical \( \sigma-\varepsilon \) curves of p(S-F)87/13 SEBS and p(S-E)87/13 PDMS are plotted in Figure 4. The different trend of the curves was indicative of the different mechanical behaviour of the two elastomers, the PDMS-based coatings being characterized by lower values of stress at break and elongation at break than SEBS-based coatings (Table 1). Moreover, the value of elastic modulus \( (E) \) evaluated for PDMS \( (E = 0.13 \pm 0.06 \text{ MPa}) \) was one order of magnitude lower than that for SEBS \( (E = 3.94 \pm 0.34 \text{ MPa}) \). There was no significant change in modulus for coatings containing the copolymer, being \( E = 0.23 \pm 0.14 \text{ MPa} \) for p(S-E)87/13 PDMS and \( E = 2.35 \pm 0.65 \text{ MPa} \) for p(S-E)87/13 SEBS. Thus, the deposition of a 2 µm layer of a matrix/copolymer blend (93/7 wt/wt) on a 150–200 µm thick sample of matrix material did not affect the bulk mechanical properties of the free-standing polymer films. This finding supports previous results for films prepared by direct incorporation of the copolymer in a thicker layer of polymer matrix (Marabotti et al. 2009).

![Stress–strain curves for p(S-E)87/13_SEBS (a) and p(S-E)87/13_PDMS (b).](image-url)

Figure 4. Stress–strain curves for p(S-E)87/13_SEBS (a) and p(S-E)87/13_PDMS (b).
Table 1. Tensile test results for PDMS- and SEBS-based coatings and the corresponding matrices.

| Coating         | $E^a$ (MPa) | $\sigma_{\text{max}}^b$ (MPa) | $\epsilon_{\text{max}}^c$ (%) |
|-----------------|-------------|-------------------------------|-------------------------------|
| SEBS            | 3.94 ± 0.34 | 5.93 ± 0.82                   | 930 ± 67                      |
| p(S-E)87/13_SEBS| 2.35 ± 0.65 | 7.46 ± 2.07                   | 1040 ± 53                     |
| PDMS            | 0.13 ± 0.06 | 0.20 ± 0.05                   | 201 ± 98                      |
| p(S-E)87/13_PDMS| 0.23 ± 0.14 | 0.32 ± 0.05                   | 115 ± 33                      |

$c$: Not accurate, decreasing with time.
$d$: Not determined.

Static contact angle and surface tension of the coatings

The static contact angles of PDMS and SEBS matrices, their respective coatings and pristine polymers were determined using two wetting liquids, water and n-hexadecane (Table 2).

SEBS-based coatings were found to be hydrophobic ($\theta_w \geq 102^\circ$) and partially lipophobic ($\theta_h \geq 38^\circ$). The inclusion of the fluorinated copolymer in the top layer especially affected the lipophobic character of the coatings, with $\theta_h$ larger than that of SEBS. This result is in agreement with previous data for amphiphilic SEBS films (Martinelli et al. 2008). On the other hand, $\theta_w$ was generally similar to that of the SEBS matrix and higher only in the case of p(Si-F)83/17_SEBS with a large mole percentage of F units. PDMS-based coatings exhibited large contact angles with water ($\theta_w \geq 105^\circ$). The contact angles with n-hexadecane were generally low ($\theta_h \leq 40^\circ$) and tended to decrease with time as a consequence of the greater lipophilicity of the matrix and the copolymer.

To extract solid surface tension values from the experimental $\theta$ values, Equation 2 was used following the Owens–Wendt–Kaelble approach. The surface tensions $\gamma^a$ calculated for the coatings, the respective copolymers and the SEBS and PDMS controls are also presented in Table 2. Despite their partial lipophobicity, SEBS-based coatings displayed substantially lower surface energies (18.9 mN m$^{-1}$ $\leq \gamma^a \leq 22.7$ mN m$^{-1}$) than that of the matrix (25.4 mN m$^{-1}$). This suggests that the surface-active copolymer was segregated at the polymer–air interface, driven there by the lowest surface energy component, whether F or S. This behaviour was more marked for coatings containing the fluorinated copolymer, for which the $\gamma^a$ values slightly decreased with increasing F content. PDMS-based coatings displayed a more complex behaviour and a trend of $\gamma^a$ with copolymer composition was not observed, even though the $\gamma^a$ values were characteristic of films with a low surface energy (21.8 mN m$^{-1} \leq \gamma^a \leq 24.7$ mN m$^{-1}$) very similar to that of the PDMS control ($\gamma^a = 23.3$ mN m$^{-1}$). In any case, the dispersion component of $\gamma^a$ provided a predominant contribution ($\gamma^d \geq 18.6$ mN m$^{-1}$), with the polar component being generally minimal ($\gamma^p \leq 1.3$ mN m$^{-1}$), and extremely low for PDMS-based coatings ($\gamma^p \leq 0.3$ mN m$^{-1}$). This behaviour is typical of low surface tension, apolar polymer surfaces.

Surface composition of the coatings

Atomic surface compositions for the coatings were determined at two photoemission angles $\phi$ of 70° and 20° by angle-resolved XPS. Experimental data are summarized in Table 3, where they are also compared with the theoretical values for the respective parent polymers and blends. SEBS-based coatings containing the F component showed a surface enriched in fluorine (4.9% for p(S-F)83/17_SEBS and 13.0% for p(S-F-E)56/18/26_SEBS at $\phi = 70^\circ$) compared to the theoretical percentages calculated for the corresponding polymers.

Table 2. Contact angles and surface tensions for PDMS- and SEBS-based coatings and the corresponding neat copolymers and matrices.

| Coating         | $\theta_w^a$ ($^\circ$) | $\theta_h^b$ ($^\circ$) | $\gamma^d$ (mN m$^{-1}$) | $\gamma^p$ (mN m$^{-1}$) | $\gamma^a$ (mN m$^{-1}$) |
|-----------------|------------------------|------------------------|--------------------------|--------------------------|--------------------------|
| SEBS            | 102 ± 2                | 26 ± 1                 | 24.8                     | 0.6                      | 25.4                     |
| p(S-F)83/17_SEBS| 110 ± 1                | 50 ± 2                 | 18.6                     | 0.3                      | 18.9                     |
| p(S-F)87/13_SEBS| 103 ± 1                | 38 ± 2                 | 21.9                     | 0.8                      | 22.7                     |
| p(S-F-E)56/18/26_SEBS | 102 ± 1            | 48 ± 1                 | 19.3                     | 1.3                      | 20.6                     |
| PDMS            | 110 ± 1                | 33 ± 2$^c$             | 23.3                     | 0.0                      | 23.3                     |
| p(S-F)83/17_PDMS| 105 ± 1                | 29 ± 1$^c$             | 24.4                     | 0.3                      | 24.7                     |
| p(S-F)87/13_PDMS| 109 ± 1                | 40 ± 1$^c$             | 21.6                     | 0.2                      | 21.8                     |
| p(S-F-E)56/18/26_PDMS | 109 ± 1            | 39 ± 1$^c$             | 22.0                     | 0.1                      | 22.1                     |
| p(S-F)83/17$^d$ | 104 ± 1                | ~ 0$^d$                | nd$^e$                   | nd$^e$                   | nd$^e$                   |
| p(S-F)87/13$^d$ | 100 ± 1                | ~ 0$^d$                | nd$^e$                   | nd$^e$                   | nd$^e$                   |
| p(S-F-E)56/18/26$^d$ | 109 ± 1            | ~ 0$^d$                | nd$^e$                   | nd$^e$                   | nd$^e$                   |

$a$: Measured with water and n-hexadecane.
$b$: Calculated with the Owens–Wendt–Kaelble method: $\gamma^d$ dispersion component, $\gamma^p$ polar component.
$c$: Not accurate, decreasing with time.
$d$: Films prepared by spin-coating a 3% (wt/v) solution in toluene (or TFT) and evaporated at room temperature for 12 h and at 120°C for 12 h.
$e$: Not accurate, because of wetting.
$f$: Not determined.
Besides fluorine, the surfaces contained carbon, oxygen and silicon, indicating that the F, E and S co-units of the amphiphilic copolymer simultaneously populated the surface. In particular, the surfaces were enriched in oxygen, while silicon and carbon contents were lower with respect to the theoretical composition. Similarly, the surface of PDMS-based coatings containing F co-units was enriched in fluorine and its atomic percentage changed with $\phi$, consistent with a composition gradient along the polymer surface normal. The fluorine percentage decreased with increasing sampling depth (eg it passed from 10.0% to 4.5% in going from $\phi = 70^\circ$ to $\phi = 20^\circ$ for p(S-F-E)56/18/26_PDMS). Moreover, the oxygen and silicon percentages were larger than and similar to the theoretical values, respectively, confirming the selective segregation of the polymer at the polymer–air interface. Notably, the experimental values of fluorine in F co-unit containing surfaces and of oxygen in E co-unit containing surfaces were greater than those evaluated for the respective copolymers and blends, regardless of the polymer matrix used.

An angle-resolved XPS analysis was also carried out on the coatings after immersion in water for 7 days, with the aim of ascertaining whether the surface of the coatings could undergo surface reconstruction. The surface composition of the coatings after immersion is expected to be that corresponding to a kinetically trapped condition, rather than the equilibrium state when in contact with water. The XPS spectra of the surface after immersion can, therefore, be considered indicative of the chemical composition when the surface is in contact with water. The elemental analysis showed that composition varied with $\phi$ and the fluorine atomic percentage followed the same trend discussed for the surfaces before immersion in water. For SEBS-based coatings, it was found that the composition of the surface changed only slightly after immersion in water. A similar behaviour was also shown by the fluorine-free p(S-E)87/13_PDMS coating. By contrast, PDMS coatings containing a fluorinated polymer displayed a more marked reconstruction after immersion in water with a significant decrease in fluorine content (eg from 10.0% before immersion to 4.9% after immersion, at $\phi = 70^\circ$ for p(S-F-E)56/18/26_PDMS).

### Settlement of zoospores of U. linza

The mean density of spores settled (attached) on the test surfaces is shown in Figure 5. All the PDMS-based coatings had a lower density of spores than the PDMS control, although p(S-F)83/17_PDMS was not significantly different to the PDMS control ($p > 0.05$). Settlement was typically lower on the SEBS-based coatings than on the PDMS coatings. All the SEBS-based coatings had a higher density of spores than the SEBS control, but a significant difference was only observed for the sample p(S-E)87/13_SEBS ($p < 0.05$).
Attachment strength of sporelings of *U. linza*

The settled spores germinated and grew well on all coatings and after 7 days a green lawn of sporelings covered all of the surfaces, including those that had a lower initial density of settled spores. Sporeling biomass data are shown in the Supplementary information. The mean percentage of biomass removed after exposure to a wall shear stress of 52 Pa is shown in Figure 6. The percentage removal from all of the PDMS-based coatings was higher than that from the PDMS control. Notably, the amphiphilic coatings p(S-E)\textsubscript{87/13}PDMS and p(S-F-E)\textsubscript{87/13}PDMS showed >70% removal, and were significantly different ($P<0.05$) to the PDMS control, which only had <20% of the biomass removed. By contrast, all of the SEBS-based coatings showed poor release of sporelings, all having lower percentage removal (5.9% to 15.5%) than the SEBS control (28.3%).

Discussion

Novel amphiphilic copolymer and terpolymer samples (p(S-F)\textsubscript{83/17}, p(S-E)\textsubscript{87/13} and p(S-F-E)\textsubscript{56/18/26}) were synthesized and used for the preparation of SEBS- and PDMS-based coatings, in order to compare the bulk mechanical, surface and biological properties of the coatings based on the two elastomer matrices. The polymers were designed to have at least a constituent capable of acting as compatibilizer between the polymer and the matrix. For this reason, a novel styrene monomer carrying a siloxane side chain (S) was synthesized and copolymerized with a fluoroalkyl (F) and/or an ethoxylated (E) styrene monomer. The polystyrene main backbone and the relatively long polysiloxane side chains were anticipated to favour the dispersion of the polymer in both matrices. In no case was macroscopic phase separation detected of any copolymer from either matrix. Moreover, the simultaneous presence of the S, F and/or E side chains allowed the hydrophobic/hydrophilic balance of the final amphiphilic polymer to be easily tuned.

The elastomeric character of the SEBS-based coatings was inherent in the physically cross-linked structure of the block copolymer matrix. Elastomeric PDMS-based coatings were chemically cross-linked by a condensation curing reaction of the PDMS matrix that required a metal catalyst to occur. Unlike previous work (Martinelli, Sarvothaman, Galli et al. 2012), the catalyst of choice was here bismuth neodecanoate. It has been shown that such bismuth-catalysed PDMS coatings are not toxic in laboratory assays against several marine species (Pretti et al. 2013).

For a better comparison of the coating systems, two sets of films were prepared according to the same two-layer geometry which consisted of a thin top layer of a blend between the polymer (7 wt%) and the matrix (SEBS or PDMS) deposited on a thicker bottom layer of the matrix alone. This strategy is widely used for SEBS-based coatings, even though the content of the copolymer incorporated in the top layer was much higher (90–100 wt%) (Krishnan et al. 2006; Martinelli et al. 2008; Weinman et al. 2009; Cho et al. 2011). By contrast, this approach is essentially new for the preparation of PDMS-based coatings, for which a one-layer strategy is generally reported consisting of the dispersion of a
layer coating, even when a lowest surface energy expected to be facilitated in a thin top layer of a two-layer coating, even when a lowest surface energy fluorinated component is replaced by a comparatively high surface energy component, eg the siloxane side chain in p(S-E)87/13. This geometry allowed the independent control of the bulk thickness and elastic modulus properties on one hand, and the surface and interface properties on the other hand, with the use of a low amount of a surface-active polymer. It is widely stated that bioadhesion of hard fouling organisms is proportional to \((E\gamma)^{1/2}\), where \(E\) and \(\gamma\) are the elastic modulus and the surface tension of the coating, respectively (Brady & Singer 2000). In particular, low adhesion corresponds to low elastic modulus because the mobility of the low modulus surface allows the bioadhesive to slip during interfacial failure (Brady 1999). The elastic modulus was also shown to play an important role in the detachment of *U. linza* sporelings at a 52 Pa shear stress from PDMS coatings. A removal of 80% of sporelings was achieved for low modulus \((E = 0.2\) and 0.8 MPa) coatings, whereas almost no release was observed for the highest modulus \((E = 9.4\) MPa) coating tested (Chaudhury et al. 2005). Furthermore, the removal of sporelings was significantly reduced at \(E = 2.7\) MPa. Thus, it would be expected that the modulus recorded for SEBS-based coatings \((E = 2.3-3.9\) MPa) in the present study would only permit a low release.

The thickness of the coating is another important parameter in release of foulers (Brady & Singer 2000). Chaudhury et al. (2005) also demonstrated that removal of sporelings of *U. linza* was significantly improved for a coating of 100 Hm or higher compared to 16 Hm. Following this rationale, elastomeric films were prepared with an overall thickness of 150-200 Hm. Moreover, SEBS-based coatings as well as PDMS-based coatings exhibited generally low surface tensions \((18.9\ \text{mN m}^{-1} \leq \gamma_S \leq 24.7\ \text{mN m}^{-1})\), due to the migration of the lower surface energy component (S or F) to the polymer air–interface. In particular, XPS analysis of the blend coatings containing any surface-active polymers revealed that their surface was greatly enriched in fluorine and oxygen contents, with these being even higher than the theoretical values calculated for the blends and respective parent polymers. Such enrichment was especially significant for the F co-unit containing coatings. Possibly the surface-active polymer saturated the outer layers and its surface tension dictated the surface energy behaviour of the coating. The two sets of coatings differed in surface chemical composition, due to a different effectiveness in the surface segregation of the polymers from the matrix. This may be reflected in their different response to the external environment. While the chemical composition of SEBS-based coatings remained essentially stable after immersion in water for 7 days, the PDMS-based coatings, especially those containing either fluorinated polymer, changed, there being a significant reduction in fluorine content. This suggests a more marked amphiphilic nature of the latter coatings.

In general, SEBS-based and PDMS-based coatings showed different biological properties against the macroalga *U. linza*. Specifically, all the PDMS-based films reduced the density of settled spores compared to the PDMS control and coatings containing ethoxylated units were more effective than those with fluorinated units. This finding is in agreement with previous results, which showed that experimental coatings containing ethoxylated chains inhibited spore settlement (Krishnan et al. 2006; Wang, Pitet et al. 2011). SEBS films exhibited lower spore settlement compared to PDMS coatings, which is consistent with the observation that high densities of spores generally settle on PDMS elastomers (Bennett et al. 2010).

Surprisingly, at an applied shear stress of 52 Pa, SEBS and PDMS controls were found to exhibit similar release of sporelings of *U. linza*, which is not what would be expected on the basis of their elastic modulus (Chaudhury et al. 2005). However, if higher shear stress values had been applied, it is likely that differences would have been seen as shown in Weinman et al. (2009). The shear stress used in the present experiment was chosen to maximize the differences in release from the coatings containing the surface-active polymers. PDMS-based coatings demonstrated higher release of sporelings with respect to the corresponding SEBS-based coatings. The inclusion of the copolymers has positive effects only for PDMS coatings, while no significant improvement in SEBS coatings was detected with respect to their own control. These findings suggest that the 10-fold lower elastic modulus of PDMS-based coatings resulted in enhanced FR efficacy. However, ascribing such big differences in biological performances solely to the mechanical properties appears simplistic and the compositional effects of the outer surface have to be considered. The same copolymer blended with the two elastomers generated very different surfaces. In particular, PDMS coatings after immersion were found to be richer in oxygen and silicon and poorer in carbon and fluorine with respect to the corresponding SEBS coatings. The presence of the ethoxylated chains in the PDMS-based coatings also favoured the release of sporelings of *U. linza*, p(S-E)87/13_PDMS being the best performer (release of 90%) not containing the fluorinated component.

To the authors’ knowledge, the present study is the first to compare the mechanical, surface and FR properties of SEBS- and PDMS-based coatings containing the same amphiphilic polymer. It is suggested that the supe-
rior biological properties of PDMS-based coatings depended on the synergistic effect of the low elastic modulus of the matrix combined with the chemical composition of the surface after preferential surface-segregation of a suitable surface-active polymer. PDMS-based coatings containing polyethylene glycol chains were found to exhibit much higher release of sporelings of *U. linza* than those containing fluorooalkyl chains.

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