

SF4	0.2	0.3	1.1	1.2
SF20	0.3	0.4	0.7	1.2
SF50	0.2	0.6	1.1	1.4
SF9P1	0.4	0.7	1.1	1.4
SF8P2	0.5	0.9	1.1	1.4
SF6P4	0.5	0.9	1.2	1.4

^{a)} Calculated by Eqn. 1.

3.3. Contact angles and surface tension

Water (θ_w) and *n*-hexadecane (θ_h) contact angles measured for the two-component and three-component films are collected in Table 3.

S0 films, not containing the surface-active additives, showed a hydrophobic ($\theta_w = 110^\circ \pm 3^\circ$) and lipophilic ($\theta_h = 37^\circ \pm 1^\circ$) nature, consistent with the wettability of other polysiloxane films [49,50]. SPy films were characterised by θ_w and θ_h values slightly lower than or similar to those of S0, suggesting that the polymer surface was preferentially populated by polysiloxane chains. For SF x films, θ_w appeared to slightly increase with the content of F, passing from 106° for SF2 to 111° for SF50, even though this difference was not significant. This trend was much more evident for θ_h , as an increase by 36° was recorded in going from SF2 to SF50 ($76^\circ \pm 1^\circ$). These results show that the perfluoroalkyl chains were segregated at the film surface and confirm that *n*-hexadecane is more able than water to better discriminate between fluorine- and silicon-rich surfaces [45].

The surface tension (γ_s) of the films was evaluated by the two additive-component method of Owens-Wendt-Kaelble [34,35]. The films exhibited relatively low γ_s values in the range of 11.9–23.8 mN m⁻¹ (Table 3). Most of the test films displayed γ_s values very similar to that of the polysiloxane matrix S0, regardless of the chemical composition of the top layer. Only SF10–SF50 exhibited significantly lower surface tensions as a consequence of increases recorded in both θ_w and θ_h . For the three-component films, even for those containing the higher amounts of F, γ_s was in the high value range. **The values of θ_w , and consequently of γ_s , for polymer films are influenced by several surface factors, especially the surface chemical heterogeneity of amphiphilic polymers in which the different chemical constituents may exhibit opposed responses to the interrogating liquids [51,52]. Thus, in these three-component films the intrinsic tendency of the fluoroalkyl chains to decrease the surface tension was partly compensated by the simultaneous presence of the polyoxyethylene chains that are**

by contrast prone to increase it. The surface segregation of the surface-active components was in fact confirmed by the AR-XPS measurements (see below).

Table 3

Contact angles^{a)} and surface tensions^{b)} of films before and after immersion in water for 14 days.

Film	Before			After		
	θ_w (°)	θ_h (°)	γ_s (mN m ⁻¹)	θ_w (°)	θ_h (°)	γ_s (mN m ⁻¹)
S0	110±3	37±1	22.4	103±1	30±2	24.6
SP2	103±3	36±1	23.3	107±2	37±2	22.6
SP4	106±2	37±1	22.7	108±1	37±1	22.5
SP10	113±3	35±1	22.9			
SF2	106±2	40±2	22.0	109±2	40±1	21.7
SF4	108±2	40±2	21.8	108±3	40±1	21.8
SF10	110±3	74±2	12.6			
SF20	108±2	71±1	13.7	109±2	67±3	14.5
SF50	111±1	76±1	11.9	101±4	71±2	15.5
SF9P1	106±1	36±1	22.9	109±2	36±1	22.7
SF8P2	101±2	35±1	23.8	108±1	35±1	23.0
SF6P4	105±2	35±1	23.3	108±1	35±1	23.0

^{a)} Measured with water and *n*-hexadecane. ^{b)} Calculated with the Owens Wendt-Kaelble method.

To monitor contact angles as a function of exposure time to water, the films were kept immersed in deionised water and θ_w and θ_h were measured at different time intervals up to 14 days (Table 3). Both θ_w and θ_h were not significantly affected by the relatively long immersion time. As a result, γ_s did not change with immersion in water. One exception was SiF50, which showed a notable drop in both θ_w and γ_s , possibly due to the hiding from water of the perfluoroalkyl chains away from the highly fluorine-enriched film surface.

3.4. Surface chemical composition

Atomic surface compositions of the films were determined at two photoemission angles ϕ of 70° and 20° by AR-XPS. The experimental data at different ϕ for the atomic surface compositions from the signals centered at 290 eV (C(1s)), 533 eV (O(1s)), 689 eV (F(1s)) and 153 eV (Si(2p)) are summarised in Table 4. Only the two-component and three-component films with a F content > 4 wt% revealed fluorine at the surface. In these cases, fluorine percentage was higher than that expected on the basis of the nominal amount of F additive in the

top layer formulation, being even larger than or comparable to the theoretical percentage calculated for the SF10 containing the highest F content. However, the effectiveness of fluorine surface segregation depended on the presence of the P comonomer. In fact, by comparing SF8P2 and SF10 possessing a similar nominal amount of F, one notes that the experimental fluorine percentage was much less for SF8P2 (< 8% vs. > 23%), containing the P additive. Thus, the polymer surfaces of three-component formulations were also populated by the polyoxyethylene chains. Accordingly, SP4 was enriched in carbon and oxygen with respect to the theoretical composition, indicating that the polyoxyethylene chains were exposed to the polymer–air interface, as a consequence of their covalent linkage to the lower surface energy components S and F.

Table 4

AR-XPS atomic composition of two-component and three-component films before and after immersion in water for 7 days.

Film	ϕ (°)	Before				After			
		C (%)	O (%)	Si (%)	F (%)	C (%)	O (%)	Si (%)	F (%)
SP4 ^{a)}	70	51.9	26.1	22.0	–	53.3	26.8	19.9	–
	20	52.5	26.9	20.6	–	53.6	27.0	19.4	–
SF2	70	52.7	25.6	21.7	nd ^{b)}				
	20	51.8	27.1	21.1	nd ^{b)}				
SF4	70	55.2	24.9	19.9	nd ^{b)}	52.6	25.6	21.8	nd ^{b)}
	20	53.0	25.5	21.5	nd ^{b)}	53.5	25.6	20.9	nd ^{b)}
SF10 ^{a)}	70	42.5	19.8	14.4	23.3				
	20	41.4	18.8	14.0	25.8				
SF8P2	70	48.0	24.1	20.5	7.4	52.1	26.8	21.1	nd ^{b)}
	20	49.1	26.3	18.9	5.7	61.5	27.3	11.1	0.1
SF6P4	70	45.7	25.5	23.0	5.8	56.6	26.1	15.9	1.4
	20	51.9	25.3	18.7	4.1	58.5	29.5	10.5	1.5

^{a)} Theoretical atomic percentage calculated on the basis of the nominal composition of the top layer formulation. For SP4: Si ~ 24%, C ~ 51%, O ~ 25%; for SF10: Si ~ 23%, C ~ 49%, O ~ 22%, F ~ 6%. ^{b)} Not detected.

An AR-XPS analysis was also carried out on the samples after immersion in water for 7 days, with the aim of ascertaining whether the surface of the films could undergo surface reconstruction. All the films containing the P additive appeared to be enriched in carbon and oxygen after immersion in water, especially

the three-component formulations for which increases in carbon and oxygen surface contents were accompanied by significantly decreased amounts of silicon and fluorine (Table 4). Such a chemical modification of the surface was attributed to the migration of the hydrophilic P surface-additive to the polymer–water interface, owing to the enthalpic gain associated with a better solvation of the polyoxyethylene chains.

3.5. Ecotoxicological assays

Prior to assaying the films as AF/FR coatings, an ecotoxicological study was carried out based on the leachates of the S0 films. The final goal was to ascertain the incidence of ecotoxicological effect of the TBAF on two different model organisms, the bacterium *Vibrio fischeri* and the alga *Dunaliella tertiolecta*. Conservatively, these experiments were conducted radicalizing the leaching conditions in order to foster the release of the potentially toxic molecules, towards the test microorganisms. Indeed, the surface/volume ratio was increased up to 395 cm² L⁻¹ in these tests, rather than the 10 cm² L⁻¹ that is generally used with PDMS-based films [33,39].

V. fischeri: inhibition of bioluminescence. Ecotoxicity of the leachates was monitored as the decrease in the bioluminescence ($\lambda = 490$ nm) of *V. fischeri* by a screening test (15 min of incubation and 100% leaching, without further dilution). The leachates of the S0 films showed a low percentage of effect (6.5 ± 0.8 %) comparable to that of the control (5.4 ± 0.4 %) (Figure 2). These results pointed to the absence of ecotoxicity against *V. fischeri*. Therefore, the full test of the ecotoxicological parameters EC_{20/50} was not performed.

D. tertiolecta: inhibition of growth. The growth inhibition of *D. tertiolecta* cells (cells L⁻¹) was evaluated after 72 h of exposure to leachates (100% without dilutions) (Figure 2). The algal growth of the control was increased by a factor 16 with respect to the beginning, which proves that the cells were viable and the test was significant. The S0 films presented almost the same algal growth, comparable with the one on the glass control without significant difference in statistics between the films. This result pointed out the absence of ecotoxicity of the test films.

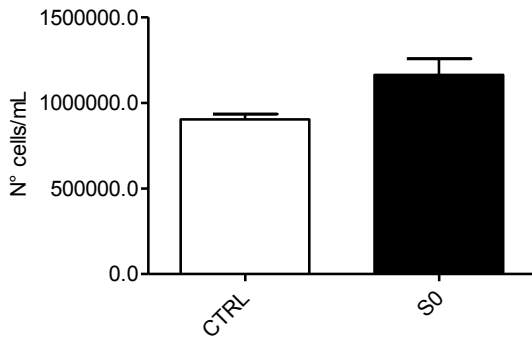
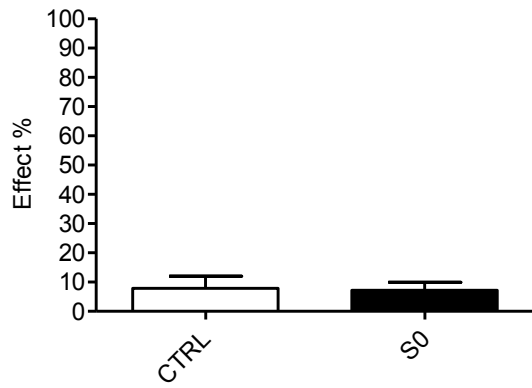


Fig. 2. Ecotoxicity tests on S0 and control: bioluminescence inhibition of *V. fischeri* (top), and growth inhibition of *D. tertiolecta* (bottom).

3.6. Biological tests

In the settlement (adhesion) test competent larvae of *F. enigmaticus* were directly pipetted on the polymer surfaces and the percentage of adhesion was evaluated after 48 h of incubation (Figure 3).

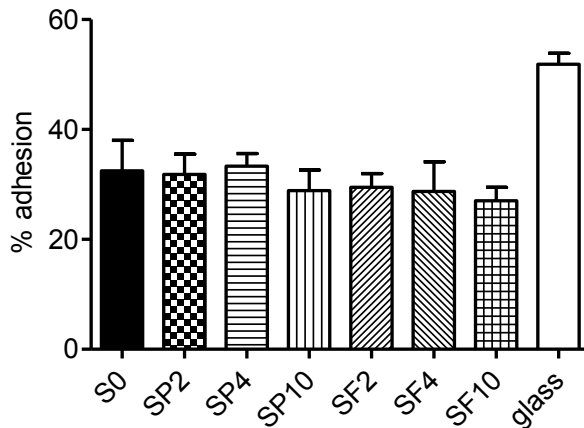


Fig. 3. Percent of adhesion of competent larvae of *F. enigmaticus* after 48 h on

two-component films SFx (2–10 wt% F) and SPy (2–10 wt% P) and silicone S0 and glass controls.

The settlement of *F. enigmaticus* on glass was markedly higher than that on polymer films (Dunn's test, $p \leq 0.001$). Settlement was found to be slightly lower on films SFx than SPy, although this difference was not significant. None of those films inhibited the adhesion of larvae significantly better than the polysiloxane control S0, indicating that the inclusion of the surface-active additive was not sufficient to improve the AF performance of the films.

18-day worms with well-formed calcified tubes (2–4 mm length) were submitted to the removal test in the turbulent channel flow apparatus. The removal percentage of *F. enigmaticus* after exposure to a wall shear stress of 24 Pa in the flow channel is shown in Figure 4.

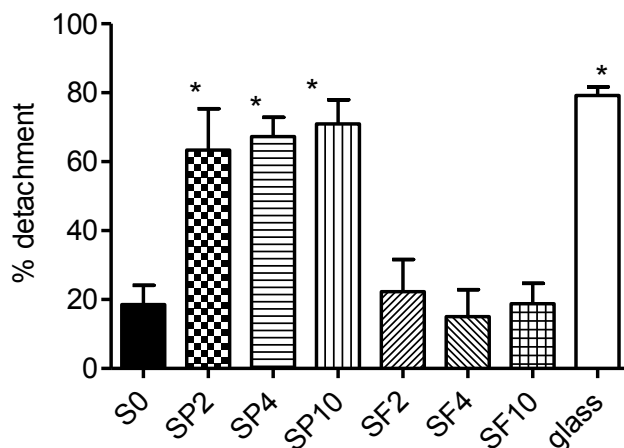


Fig. 4. Percent of detachment of calcareous tubes of *F. enigmaticus* at 24 Pa shear stress from two-component films SFx (2–10 wt% F) and SPy (2–10 wt% P) and silicone S0 and glass controls.

*significantly different from S0 ($p < 0.05$), One-Way ANOVA (Dunnett's test).

SPy samples showed a relatively high removal percentage (> 60%) significantly better than that of the corresponding SFx films and the S0 control and comparable to that of glass, taken as a positive standard for the detachment of *F. enigmaticus* [33]. Therefore, while the addition of F to the formulation worsened the FR of the serpulid, the inclusion of P improved the FR.

Amphiphilic three-component films SFxPy were also submitted to biological testing. SP4 and SF4 were chosen as examples of best and worst performing films, respectively, and tested alongside for direct comparisons. After 48 h, competent

larvae with a partially formed proteinaceous tube and modified prototroch settled on all the organic films with percentage values > 50%, the highest attachment percentage (86%) being detected for the inorganic glass control (Figure 5).

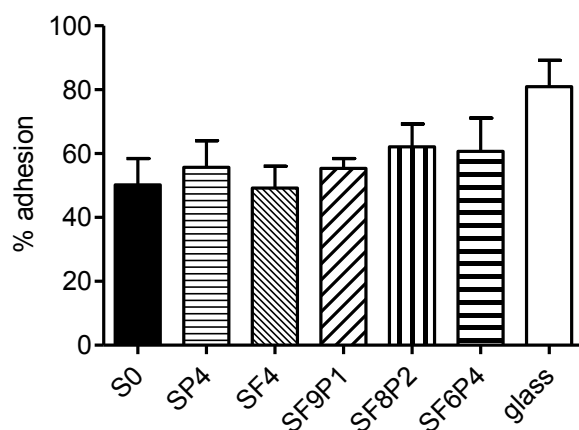


Fig. 5. Percentage of adhesion of competent larvae after 48 h on two-component films SF4 (4 wt% F) and SP4 (4 wt% P), three-component films SF_xPy (6–9 wt% F, 4–1 wt% P) and silicone S0 and glass controls. Non-parametric Kruskal Wallis test (Dunn’s post test). Films were assayed in a different batch from that of Figure 3, starting with two separate larva preparations, all derived from parent adult colony collected from the wild.

However, all the three-component films displayed similar values of adhesion percentage, without showing a significant dependence on their chemical composition. On the other hand, the relative proportion of F and P additives in the top layer formulations played a role in determining the fouling-release behaviour of the SF_xPy films. In fact, an increase in the amount of the hydrophilic additive P led to an improvement in the fouling-release properties, SF6P4 being the best performing three-component film (49% mean detachment) (Figure 6). However, from the comparison between SF6P4 and SP4 (68% mean detachment) one notes that the inclusion of the hydrophobic agent F had a negative effect on the release of tubeworms.

These findings are in agreement with previous investigations on photocross-linked PDMS-based amphiphilic films [33], where *F. enigmaticus* was found to be more easily removed from films with a larger content of hydrophilic surface-active additive. Polyoxyethylene-enriched surfaces of PDMS networks containing covalently linked surface-active additives were also found to be effective against other test organisms. Hawkins et al. [27] demonstrated that polyoxyethylenesilane amphiphiles incorporated into a PDMS matrix enhanced

the overall activity of the films against the bacterium *Bacillus* sp. 416 and the diatom *Nitzschia closterium* and a mix of both species. Stafslie et al. [28] reported that the combination of fluorinated and polyoxyethylene additives in a PDMS matrix interplayed in such a way to favour the migration of the oxyethylene chains to the polymer surface and this resulted in improved FR properties against the bacteria *Cellulophaga lytica* and *Halomonas pacifica* and reattached adults of *Balanus amphitrite*. More recently, polyoxyethylene surface-enriched amphiphilic siloxane-polyurethane coatings were proven to show excellent FR performance toward the bacterium *C. lytica*, the diatom *Navicula incerta* and the green alga *U. linza*, demonstrating comparable or superior efficacy to several commercial amphiphilic FR coatings [53].

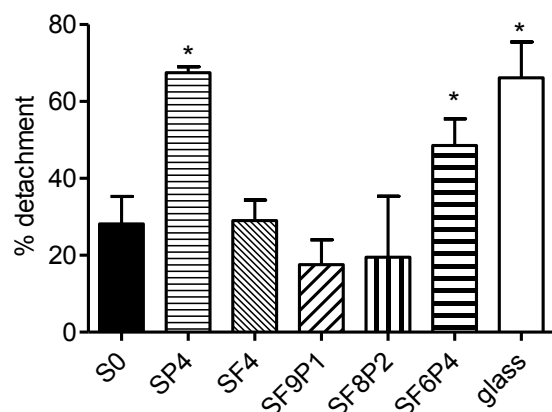


Fig. 6. Percentage of detachment of calcareous tubes at 28 Pa shear stress from two-component films SF4 (4 wt% F) and SP4 (4 wt% P), three-component films SF_xPy (6–9 wt% F, 4–1 wt% P) and silicone S0 and glass controls. *significantly different from S0 ($p \leq 0.05$), One-Way ANOVA (Dunnet's post test). Films were assayed in a different batch from that of Figure 4, starting with two separate larva preparations, all derived from parent adult colony collected from the wild.

4. Conclusions

Two-layer films were prepared by a sol-gel reaction of a difunctional silanol-terminated polysiloxane with trialkoxysilanes carrying polyoxyethylene (P) and/or perfluoroalkyl (F) chains as surface-active agents. **Incorporation of the surface-active additives affected to a significant extent the surface chemical composition of all three-component films and two-component films with a F content higher than 4%.** Thus, the effectiveness of the surface segregation of perfluorinated segments depended on the amount of F and the presence of P.

Furthermore, the outer film surface could reconstruct upon immersion in water, notably for the three-component surfaces which became more populated by P chains in response to the external environment.

The fouling-release properties against *F. enigmaticus* were especially influenced by the actual film formulation. The adult worms were more easily removed from films richer in hydrophilic P chains, the best performing films being those not containing the hydrophobic (and lipophobic) F additive. The results may provide a guidance to engineer novel surface designs for tailored application against *F. enigmaticus*, a very little investigated serpulid which would be advocated as a new model organism from the range of macrofoulants.

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