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REVIEW

Development of Environmentally Friendly Antifouling and Antimicrobial Materials

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ABSTRACT

Fouling problems have stimulated tremendous researches in the development of environmentally friendly antifouling materials. Various preparation methods have been proposed and successfully used in marine antifouling coatings. The present paper simply reviewed the main antifouling technologies such as low surface energy coatings mainly include silicone and fluorinated polymers, degradable self-polishing coatings, bio-inspired coatings with micro-nano structure surface, PEG-based antifouling coatings and other antimicrobial coatings as well as membranes coupled with nanoparticles, respectively.

KEYWORDS

Marine antifouling coating, Low surface energy, Degradable.

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INTRODUCTION

The accumulation of micro-organism and macro-organism on immersed surface, commonly referred as “fouling”, poses great threats to naval industry. Fouling increases the resistance of ship’s voyage, accelerates the hull corrosion of ship body and lead more fuel consumption, which in return increases the emission of greenhouse gases [1-3]. It is estimated that the annual maintainance cost of ship industry achieve to billions of dollars and continue to keep growing [4].

The progress of marine fouling growth can be divided into three main steps, which include the following: soluble organisms settled on the surface immersed seawater to form a conditioning film; several monads such as bacteria, diatom and protozoan anchored on the conditioning film to generate microbial biofilm or slime which provide sufficient nutrient and good environment for prokaryote, mushroom and macro-organism to grow [5,6]. The process of biological fouling [7] is showed in Fig. 1. More than 4,000 foulants species were identified [8]. The attachments of fouling organisms are influenced by marine environment such as geographical location, temperature, salinity and pH in the seawater. The colonization of foulants is also determined by substratum and hull voyage rate. Several physico-chemical parameters such as surface energy, roughness and porosity, play an important role in the adhesion of microbial on the wetted substrates [9,10]. There are two major approaches to minimize fouling which are based on either preventing biofoulants from attaching or degrading them. Traditional marine antifouling paints prevent the settlement and adhesion of fouling by releasing toxicant. However, with the increase of operating time, the toxicant release rate gradually decrease and the antifouling performance becomes increasingly inefficient [11]. In the 1970s, a durable antifouling efficiency coating called tin-based self-polishing antifouling paint was produced, which mainly used methacrylic tributyltin-ester copolymers as film-forming binder, CuO as toxicant and incorporated ZnO as filler to generate paint [12]. Tributyltin released from paint inhibits marine micro-creature from gathering onto the submerged surface up to 5 years. This type of coating can not only form a smooth film to prevent adhesion of bacteria, but also decrease fuel consumption. However, in the late 1970s, marine environmental pollution caused by tributyltin-based compound aroused a wide range of attention for researchers. Several studies showed that tributyltin-based self-polishing coating has adverse effect on marine creatures especially on oyster. Due to its toxicity and enrich-ment, in 2008, the International Maritime Organization banned the use of this kind of coating [13,14]. After that, copper-based paints and copolymers incorporated with organic booster biocides were used as alternative antifoulants to organotin antifoulants for few years. Copper is well-known as bactericide, fungicide and algicide which exhibits antifouling effect against biofouling such as barnacles and majority of algal fouling species [15]. In order to enhance its efficiency, organic booster biocides are used in combination with copper to inhibit the coalescence of fouling. However, there also exist some potential adverse effects on environment, such as, the heavy mentals in biocides can be enriched in marine organisms, which can threaten the health of human beings [16,17]. Therefore, it is urgently required to develop environmentally benign and economically viable nontoxic antifouling technologies to substitute the traditional toxic paint.

Currently, there are several catagories of environmental friendly nontoxic antifouling coatings, including tin-free self-polishing copolymer paints [18,19], low-surface-energy antifouling coatings [20,21], bio-inspired nontoxic antifouling paints, electrolytic antifouling coatings [22,23]. Now, researches develop a novel nontoxic coating with high antifouling efficiency for the purpose of preventing unwanted colonization of adhesion at interface by the following strategies: (i) Formation of microenvironment on the surface, which is difficult for fouling to survive, such as release of biocides. (ii) Formation of interface, which prevents biocontaminants from accumulating onto hull [24,25]. Herein, this review attempts to summarize the main achievements on antifouling materials and considers to give more details about nontoxic paints in the next section.

Antifouling materials

Fouling-released antifouling coatings: Low surface energy antifouling coatings mainly include silicone and fluorinated polymers, the so-called fouling-released coatings. Coatings with a very low surface free energy and modulus decreased the adhesive strength of fouling settlement which makes biofouling easily fall off when the vessel is under navigation conditions. The coatings mainly based on modifying the surface properties such as, surface wettability [26], surface hydrophobicity/hydrophilicity [27,28], surface tophography [29,30], surface free energy and surface charge [31,32]. A number of studies showed that coatings with amphiphilic properties have a high potential for antifouling coatings [33,34]. In general, when the surface free energy of coating is less than 25 mJ/m^2 or coatings exhibit water contact angles greater than 98°, the coating would possess a good antifouling performances and effectiveness of cleaning [35].

Silicone-based low surface energy antifouling coating: Silicones have been widely used for its high thermal stability, low surface tension and low glass transition temperature. In

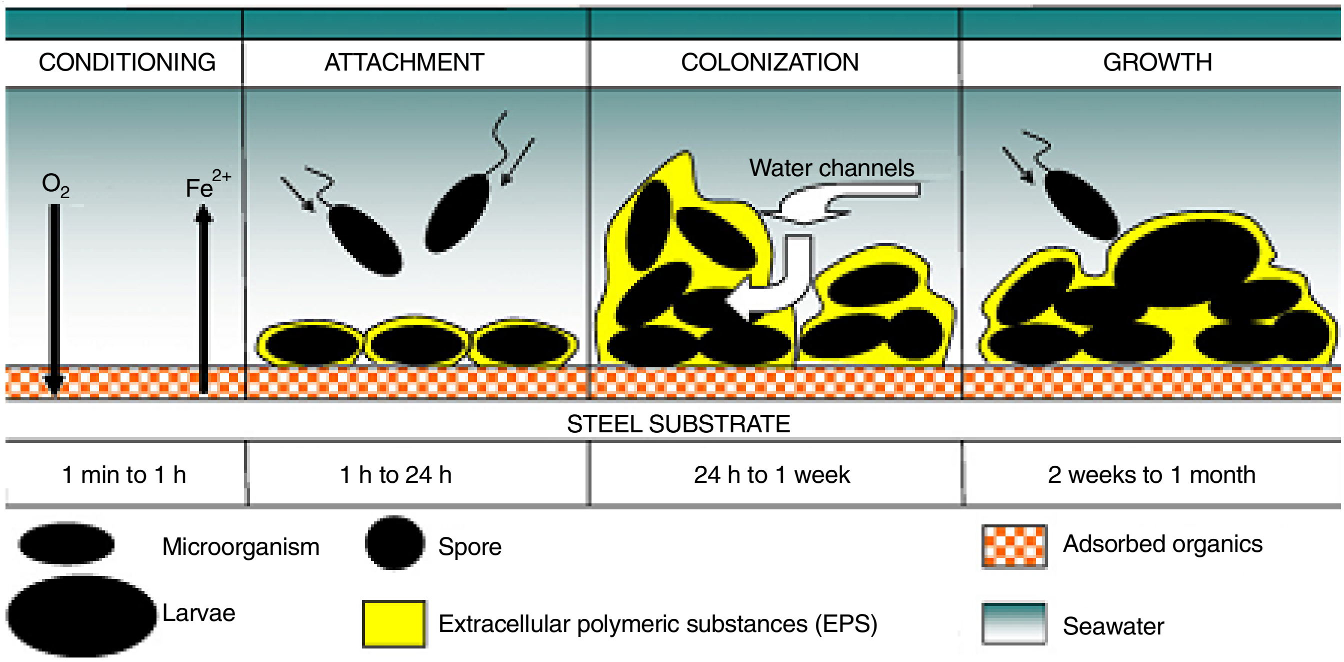


Fig. 1. Schematic of critical biofouling stages [Ref. 6]

1961, Robbart firstly succeeded in prepareing cross-linked silicones for marine coatings, the coating incorporated silicone resin largely avoids the adhesion of barnacles [36]. After that, silicone-based coatings have attracted significant scientific and economic interest over the last few decades. Schmidt and co-workers investigated the release properties of surface by using wettability measurements and adhesion testing. The contact angles (CAs) are commonly used to determine wettability and to predict adhesion, this study indicated that an optimized coating having both low water contact angle hysteresis and high receding contact angle exhibited unprecedented resistance to marine biofouling [37]. Qu *et al.* [38] have proposed a method to make composite latex consisting of a siloxane and a fluorinated copolymer *via* emulsion copolymerization. The water contact angle (θ_w) on the film increased from 106 ± 2° to 135 ± 2°.

Rath and co-workers [39] examined the effect of surface energy, modulus and surface restructuring of the coatings on the macrofouling and pseudo barnacle adhesion properties by developing two component silicone modified epoxy resin. Component A maintained 15 and 30 % silicone content and component B consisting of a polyether diamine. 30 % silicone modified epoxy coating (after gentle water wash) showed a low density of fouling after 3 months of seawater immersion, (Fig. 2). Macrofouling studies showed considerably improved foul release behaviour of the silicone modified epoxy coatings compared to the unmodified epoxy adipate coating. Polydimethylsilxane-polyure (PDMS-polyure) segmented copolymer containing fluorinated or polyhedral oligomeric silsesquioxane-functionalized (POSS-functionalized) chian extender was investigated by Fang *et al.* [40]. These authors found that all PDMS-polyurea based materials displayed stronger hydrophobic characteristics and showed a higher Ulva spores settlement but better percent removal of sporelings compared to standard PDMS elastomer (Silastic®-T2). Periodically ordered mesoporous organosilicas (PMOs) containing high density of thiol and sulfonic acid units were prepared as mesoporous nanoparticles *via* an aerosol-assisted gas-phase method and bacterial adhesion tests with *Pseudomonas aeruginosa* showed that the organobifunctional materials presented much better performance against biofilm formation [41].

Lejars *et al.* [42] described the design of hydrolyzable and hydrophobic/low-surface energy materials containing *tert*-butyldimethylsilyl methacrylate (TBDMSiMA) and poly-(dimethylsiloxane) methacrylate. Contact angles and surface energy of the graft copolymer-based are close to the value obtained for the FRC standard. Furthermore, the graft copolymers exhibited good film forming properties and erosion properties in artificial seawater which makes them suitable as new polymeric binders for hybrid self-polishing/fouling release coatings. In a recent report, Yeh and co-workers [43] modified Sylgard 184 silicone elastomer (PDMS) with a stable super-hydrophilic zwitterionic interface by covalent silanization of sulfobetaine silane (SBSi). The adherent bacteria *P. aeruginosa* and *S. epidermidis* were observed under a fluorescent microscope, which evidently showed a much lower bacterial densities (Fig. 3). They also found that the number of adherent bacteria on SBSi-modified contact lens reduced by 96.4 % compared to unmodified one and the repelling rates of PDMS-SBSi were 98 % and 97 % for bovine serum albumin (BSA) and mucin, respectively, relative to the unmodified sample. Cationic UV-curable epoxy-siloxane release coatings showed good release performance but suffered from poor coating mechanical properties, to solve this problem, a difunctional oxetane monomer (DOX), was co-photopolymerized with an epoxy-siloxane oligomer. As the DOX content increased, the Young's modulus increased due to the increased crosslink density. Besides, all DOX-toughened coatings exhibited high water contact angle (θ_w >100°) and low surface energy (12.5 mN/m-20.5 mN/m) before and after artificial seawater immersion for 50 days. For the fouling release (FR) performance of DOX-toughened coatings, all the coatings showed similar, relatively low water-jet *C. lytica* and *N. incerta* removal. However, as the DOX content decreased, the *H. pacifica* biofilm removal performance of the coatings increased [44]. They also found that DOX-toughened coatings

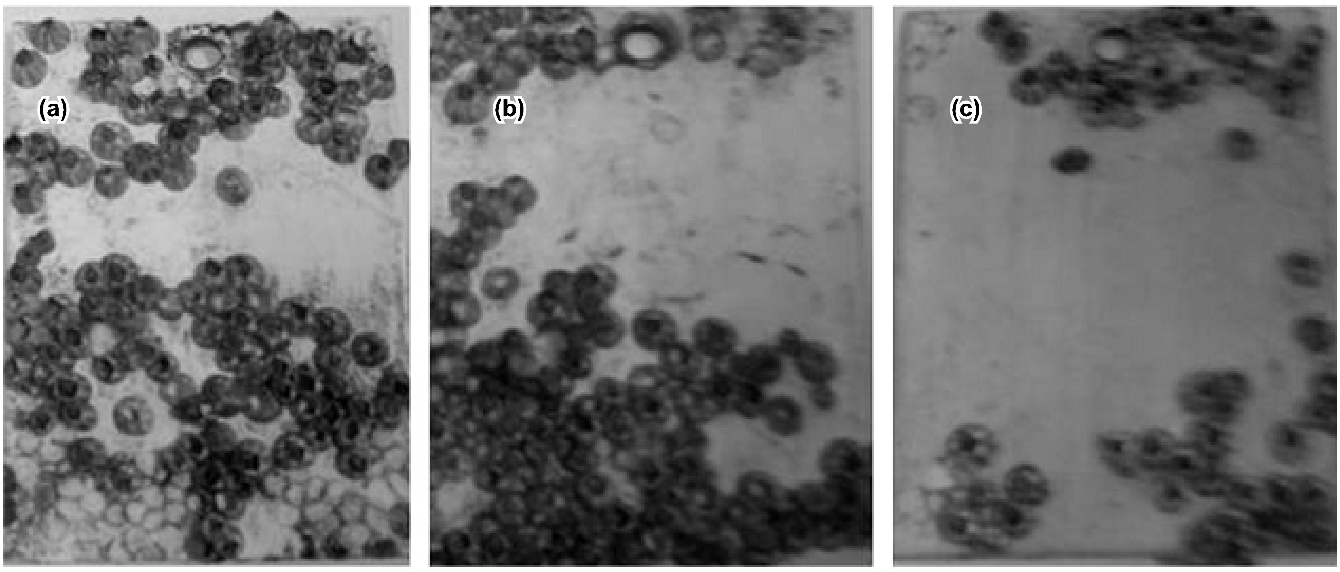


Fig. 2 Photographs of the experimental coating panels after 90 days of exposure (after gentle water wash): (A) control panel, (B) 15 % silicone modified epoxy coating, (C) 30 % silicone modified epoxy coating [Ref. 38]

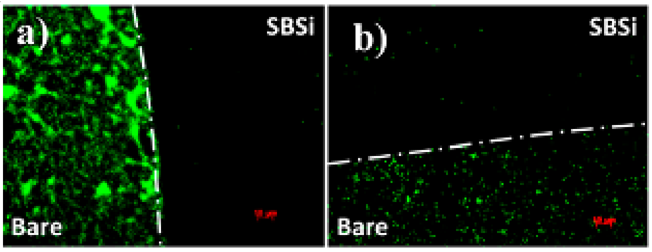


Fig. 3. Fluorescence images for *P. aeruginosa* (a) and *S. epidermidis* (b) adsorption on partially modified PDMS [Ref. 42]

(10 and 20 wt %) exhibited higher impact resistance, no leachate toxicity, enhanced mechanical properties and better overall marine fouling-release performance. Therefore, the surface properties have a significant effect on antibacterial performance.

Fluorinated-based low surface energy antifouling coatings: Fluorinated polymers have been exploited for some time with high thermal and chemical stability, low refractive index, low surface energy and high hydrophobicity [45]. Poly(1*H*,1*H*,2*H*,2*H*-perfluorodecanoyl diitaconate) film structures present a surface energy at about 7-8 mJ m^{-2} and contact angle at 88-120°. Film structure of this material showed low colonization of algae, barnacles and tubularia [46]. The cross-linked liquid perfluoropolyether (PFPE) elastomeric coatings with low surface tension, Young's modulus and contact angle hysteresis showed decreased zoospore settlement and comparable sporeling removal performance compared to PDMS elastomer standard material [47]. Martinelli *et al.* [48] reported the amphiphilic copolymers of a methacrylic monomer mixed poly(ethylene glycol) (PEG)-fluoroalkyl side chain, which were used as the surface-active components in poly(dimethylsiloxane) (PDMS) network blends at different loadings. It is found that the fluoroalkyl segments of the surface-active copolymers migrated to the outer film surface (~ 10 nm), dragging the linked PEGylated groups to the surface as well. However, the chemical composition of the films was little affected by immersion in water.

Weinman's groups [49] fabricated an amphiphilic triblock surface-active block copolymer (SABC) containing ethoxylated fluoroalkyl side chains *via* the chemical modification of a polystyrene-block-poly(ethylene-ran-butylene)-block-polyisoprene polymer (SEBS)precursor. The author found that a amphiphilic ethoxylated fluoroalkyl SABC present a high advancing contact angle ($\theta_a = 107 \pm 2°$) and a low receding contact angle ($\theta_r = 26 \pm 2°$). Bioassays were utilized to evaluate the settlement and ease of removal of two types of ubiquitous marine fouling algae, which demonstrated amphiphilic SABC showed lowest settlement density of spores of Ulva compared to PDMS and G1652 SEBS. They also found that 67 % removal of biomass at an applied water jet pressure of 24 kPa and almost complete removal at 44 kPa. As elastic modulus decresed, the release of sporelings of Ulva incresed. Weinman further investigated ether-linked surface active triblock copolymers containing poly(ethyl glycol) [Mn ≈ 500 g/mol (PEG550)] and semi-fluorinated alcohol [$CF_3(CF_2)_9(CH_2)_{10}$ (F10H10)] side chains. They found the number of cells of the diatom Navicula attached after exposure to flow decreased as the content of PEG550 to F10H10 side chains increased [50]. Zhao *et al.* [51] succeed in the synthesis of fluorinated amphiphilic copolymers consist of 2-perfluorooctylethyl methacrylate (FMA) and 2-hydroxyethyl methacrylate (HEMA) monomers, hydrophobic 2-perfluorooctylethyl methacrylate contributed to the increase in the contact angle with increased content ($\theta = 112°$, 26.7 mol % FMA), in contrast to contact angle, the incorporation of 2-perfluorooctylethyl methacrylate content resulted in the decrease in the surface free energies (γ_s = 56.2-11.4 mN/m). They also found that when the percentage of hydrophilic hydroxyl groups is increased from 4 to 7 % and hydrophobic fluorinated moieties increased from 4 to 14 % on the surface, the copolymers present favourable protein adsorpion. By using bovine serum albumin (BSA) and human plasma fibrinogen (HFg) as the proteins model, Zhao *et al.* [51] observed that hydrophobic domain inhibits a very low amount of adsorbed protein and the amount of HFg increases with the enlargement of the fluorinated domains (Fig. 4). An amphiphilic nanostructured film containing polystyrene (S) and polyoxyethylene-polytetrafluoroethylene chain side-group (Sz) was used as fouling release application [52]. The static contact angles of water (θ_w) and *n*-hexadecane

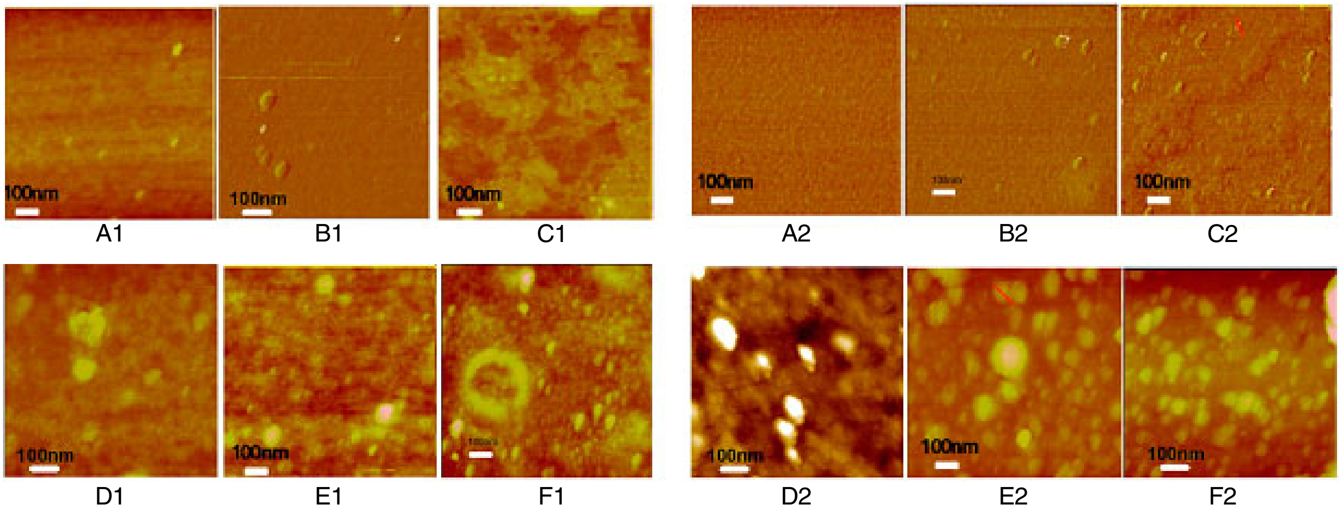


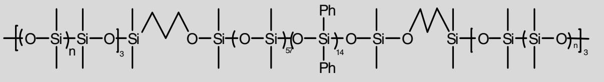
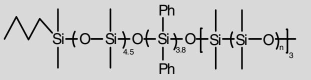
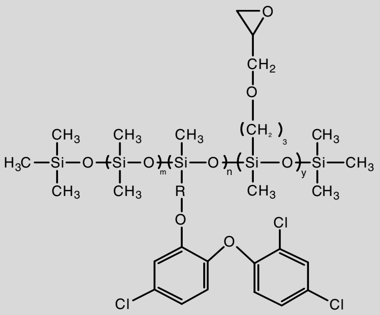
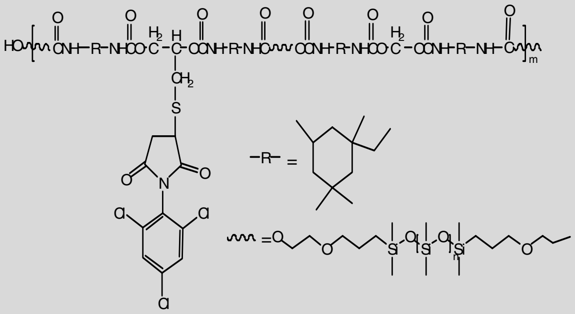
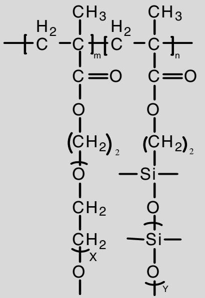
Fig. 4 AFM tapping height images of F1(A), F2(B), F3(C), F4(D), F5(E) and F6(F) film surfaces after protein adsorption, using BSA(1) and HFg(2) as the proteins model. The areas displayed are 1 µm × 1 µm [Ref. 50]

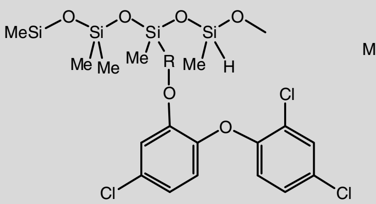
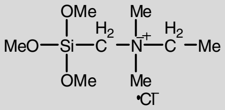
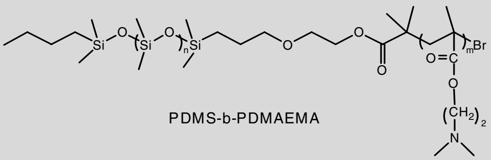
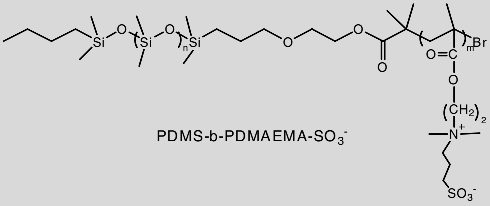
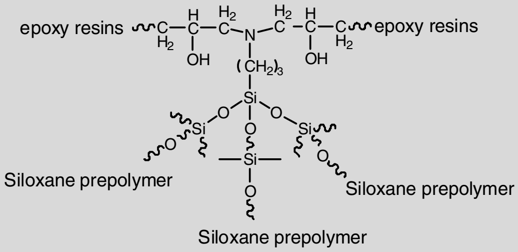
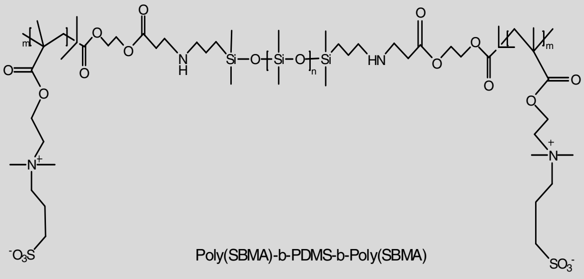
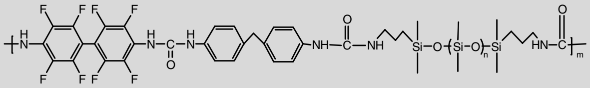
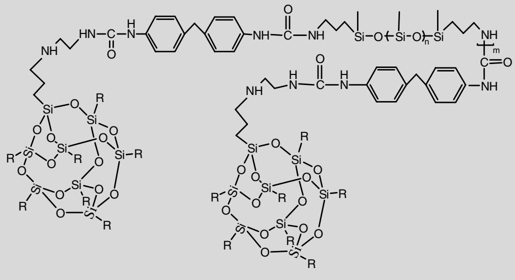
(θ_h) was tested by the sessile drop technique, with $\theta_w \geq 107°$ and $\theta_h \geq 64°$. The fluorinated film exhibited low surface tensions (13.5 mN/m $\leq \gamma_s \leq 15.3$ mN/m) contribute to hydrophobicity and lipophobicity. All the experimental surfaces showed a similar high settlement density of Ulva zoospores since the sporelings are inclined to settle on hydrophobic surface. In the meantime, the fluorinated film also exhibited a high percentage removal of UlVa sporelings after exposure to a wall shear stress of 20 Pa. Higher NaVicula cells removal was seen from S26Sz23_90 (with 10wt % SEBS) than S26Sz23_100 (with 0wt % SEBS), but there was no significant difference between S81Sz19_100 and S81Sz19_90. This phenomenon is attributed to the reason for diatom cells generally adhere weakly to hydrophilic surfaces compared to hydrophobic surfaces.

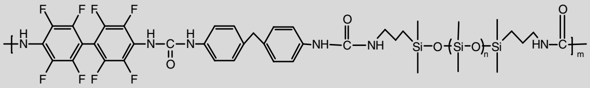
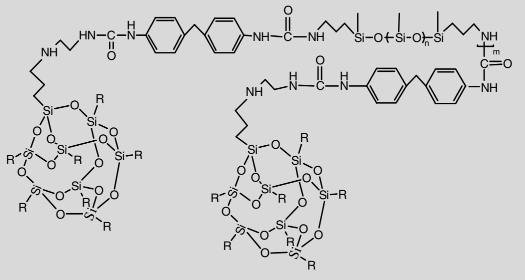
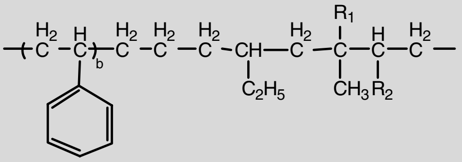
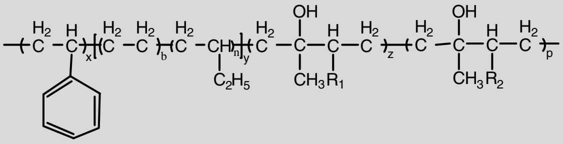
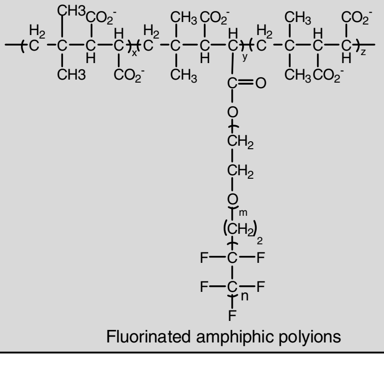
The silicone- and fluorinated-based fouling-released coatings confer a hydrophobic surface and a low surface energy in the range of 10-20 mN/m as well as long-term durability for 5-10 years but showed a weak adhesion strength of the substrate and poor mechanical properties. To solve this problm, surface modification has been widely used, but there were still has a room to develop. Herein, a simple summary of silicone-based and fluorinated fouling-released antifouling coatings is provided in Table-1.

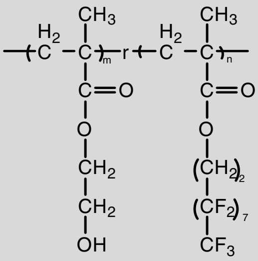
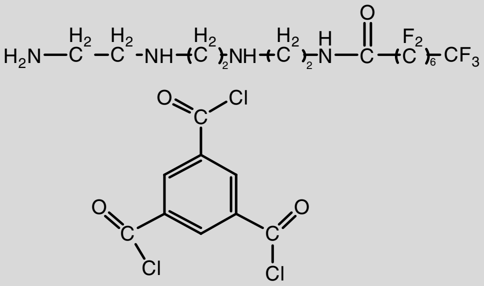
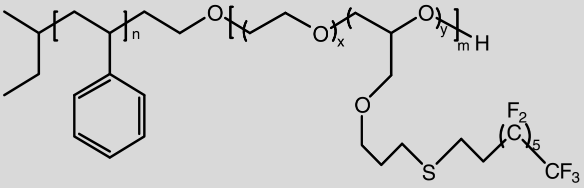
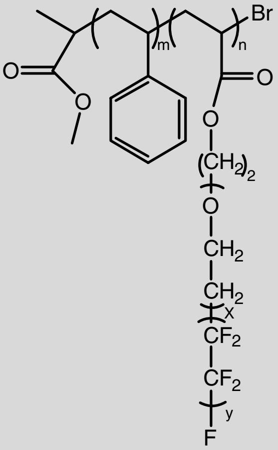
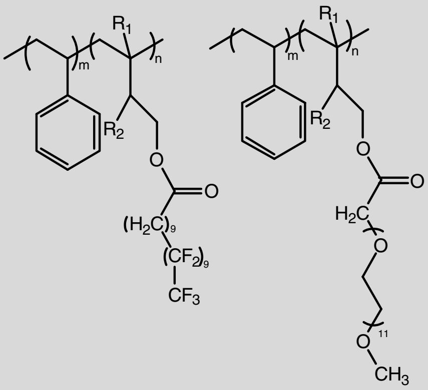
Tin-free self-polishing degradable antifouling materials: Conventional tin-free self-polishing coatings are mainly based on acrylic or methacrylic, which are easily hydrolyzable in seawater. These copolymers mixed with biocides provide a smooth surface and an ability of controlling biocide leaching rates [68]. Fouling organisms adhered to the coated surface are removed with the matrix, which is decomposed by the hydrolysis of the side groups of copolymer chains. The self-polishing antifouling materials were designed and fabricated

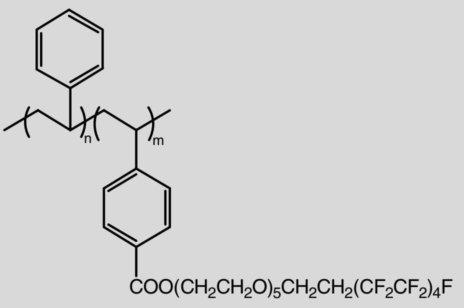
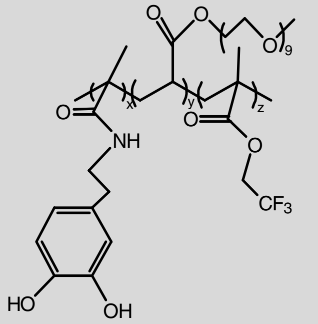
TABLE-1
SUMMARY OF SILICONE AND FLUORINATED-BASED FOULING RELEASE COATINGS

Coating	Polymer structure or units	Coating properties	Ref.
RTV11 + 10 wt % PDMSPhS oil	 RTV 11+PDMSPhS oil (Ablative)  RTV 11+PDMSPhS oil (Tethered)	↓Antifouling performance (compared to RTV11 and RTV11 + free oil) ↑Banarcle adhesion (compared to RTV11 and RTV11 + free oil) <1.0 wt % of oil leached out	[53]
Silicone + Triclosan		↓modulus, ↓the number of cross linking group ↑fouling rate, ↓modulus	[54]
PU-PDMS + N-(2,4,6-trichlorophenyl)-maleimide (TCM)		γ_S = 24-26 mJ/m^2 ↑modulus with ↑TCM antifoulant content ↓adhesion strength, the number of adhered bacterial cell, Navicula attachment and barnacle cyprids settement ↑TCM antifoulant content Marine field tests: excellent antibiofouling perfornance in 110 days	[55]
P(poly(ethylene glycol) (PEG)-r-poly (dimethylsiloxane) (PDMS))		↓surface hydrophilicity with ↑PDMS content $\theta_w < 90°$ ↓surface free energy with ↑PDMS segment γ_S = 28.2 mJ/m^2 (PDMS surface coverage: 15.1 mol %) PES/P(PEG-r-PDMS): stable and durabale antifouling properties	[56]

PDMS + triclosan(TCS) + tetradecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (C-14 QAS)	 PDMS+TCS  C-14 QAS	PDMS + TCS: 15-20 % biofilm surface coverage (12.5 and 25 wt % TCS moieties) Significant antifouling effect: 5-12.5 wt % TCS moieties PDMS + QAS: Ineffective reduction (biofilm growth of *C. Lytica)* ↑antifouling performance with ↑QAS content (*N. incerta*) ↑reduction in algal growth with ↑QAS incorporated	[57]
PDMS-b-poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA)	 PDMS-b-PDMAEMA  PDMS-b-PDMAEMA-SO$_3^-$	After 4 weeks immersion: PDMS-b-PDMAEMA: γ_S = 23.2-28.1 mN/m PDMS-b-PDMAEMA-SO$_3^-$: γ_S = 23.8-29.8 mN/m Detachment force: PDMS-b-PDMAEMA: 0.068 ± 0.018 N PDMS-b-PDMAEMA-SO$_3^-$: 0.079 ± 0.029N	[58]
Silicone/phosphorus modified epoxy coating		Salt-spray test: Corrosion resistance: siliconiled epoxy (excellent corrosion resistance) < epoxy counter parts Posess the ability for preventing the adherence and settling of marine organisms	[59]
Polyurethane + poly(sulfobetaine methacrylate)-b-poly(dimethylsiloxane)-b-poly(sulfobetaine methacrylate)	 Poly(SBMA)-b-PDMS-b-Poly(SBMA)	One month water immersion: ↑water contact angle with ↑PDMS block length ↓surface energy and pseudobarnacle adhesion strength with ↑PDMS block length Contrast: IS700, IS900, Silastic T2, PU *C. lytica* biofilm growth/ removal(water jetting: 43kPa): Lower initial biofilm growth Lower removal compared to IS900 Bacterium *H. pacifica* and unicellular microalga *N. incerta* biofilm growth/removal(water jetting: 111kPa): Higher initial biofilm growth and removal	[60]
PDMS-polyurea + fluoronated/polyhedral oligomeric silsesquioxane-functionalized segmented copolymers	 Fluotinated PDMS-polyurea segmented copolymers(A12MF)  POSS-functionalied PDMS-polyurea segmented copolymers(A12MPOSS)	Low advancing contact angle and high receding contact angle: low surface energy Contrast: glass, Silastic T2 Higher spores settlement Critical surface pressure for 50 % removal detachment of Ulva sporelings: A12MF: 23kPa A12MPOSS: 44 kPa PDMS: 62 kPa Glass: 80 kPa	[40]

PDMS-polyurea + fluotonated/polyhedral oligomeric silsesquioxane-functionalized segmented copolymers	 Fluotinated PDMS-polyurea segmented copolymers(A12MF)  POSS-functionalied PDMS-polyurea segmented copolymers(A12MPOSS)	Low advancing contact angle and high receding contact angle: low surface energy Contrast: glass, Silastic T2 Higher spores settlement Critical surface pressure for 50 % removal detachment of Ulva sporelings: A12MF: 23kPa A12MPOSS: 44 kPa PDMS: 62 kPa Glass: 80 kPa	[40]
PDMS (Sylgard 184 silicone elastomer kit) + CuO/ZnO nanoparticle		Contrast: glass, PDMS, PDMS + CuO, PDMS + CuO (CTAB), PDMS + ZnO Greater *B. fexus* attachment, higher percentage of dead cells Percentage reduction of diatom cells: PDMS + CuO: 45 ± 2 % PDMS + CuO (CTAB): 62 ± 9 % PDMS + ZnO: 59 ± 2 % 45 days field studies: SS, PDMS, PDMS + CuO, PDMS + CuO (CTAB), PDMS + ZnO Percentage inhibition of fouling: PDMS + CuO: 68 % PDMS + CuO (CTAB): 75 % PDMS + ZnO:80 %	[61]
PS-b-P(E/B)-b-PI + ethoxylated fluoroalkyl side chains	 R_1,R_2= H or $-CH_2CH_2(CH_2CH_2)_x(CF_2CF_2)_yF$ amphiphilic SABC	$\theta_{w,adv}$ = 107°, $\theta_{w,re}$ = 26° E = ~180.3MP, ~1.20.3MP (elastic modulus) Contrast: PDMS, G1652 SEBS Lowest settlement density of spores of Ulva ~67 % removal of biomass (24 MP), complete removal (44 MP) Contrast: PDMS ~51 % removal of Navicula ↓elastic modulus, ↑the release of sporelings of Ulva	[49]
PS-b-P(E/B)-b-PI + PEG550 + F10F10	 R_1= $-O(CH_2)_{10}(CF_2)_{10}$; R_2,= $-(OCH_2CH_2)_{10}(CF_2)_{12}OCH3$	$\theta_{w,adv}$ = 128°-103°, $\theta_{w,re}$ = 67°-28°, ↑amount of PEG550 and ↓amount of F10H10 Contrast: G1652 SEBS, 3-17 % attachment of F10H10 and 7-28 % attachment of PEG550 Lowest settlement densities of spores (3 % F10H10 + 28 %PEG550) 95 % removal of sporelings (24 Kpa) Contrast: MD SEBS, 0-50 % F10H10 and 0-33 % PEG550 Lowest settlement densities of Ulva(0 % F10H10 + 33 %PEG550)	[50]
LBL film + fluorinated amphiphic polyions	 Fluorinated amphiphic polyions	Contrast: silicon wafer (bare) no *Pseudomonas* coverage ↓settement of *Amphora coffeaeformits*	[62]

Poly(2-hydroxyethyl-methacrylate)-r-poly(2-prefluorooctyl)	 Fluorinated amphiphiic copolymer	↑water contact angle, ↑hydrophobic content $\theta_w = 112°$, 26.7 mol % FMA γ_S = 56.2-11.4 mN/m (↑FMA content) lowest BSA adsorption(9 % FMA content + 5 % HEMA content) lowest HFg adsorption(4 % FMA content + 7 % HEMA content) favourable protein adsorption (FMA content: 4-14 %, HEMA content: 4-7 %) Excellent antifouling ability for *Escherichia coil* adhesion)	[51]
Fluorinated polyamine + trimesoyl chloride (FPA/TMC)		$\theta_w = 88.9°$, $\gamma_S = 23.0$ mJ/m^2 superior self-cleaning and antifouling property more effective in resisting and releasing foulants such as BSA,HA and oil	[63]
Polystyrene-block-poly[(ethylene oxide)-stat-(fluocarbon-functioned allyl glycidyl ether)]	 PS-b-P(EO-stat-*f*AGE)	Constrst: Silastic T2, AEG0 Lower spore settement densities Significant enhanced fouling-release activity Essentially all of biomass removal (8 mol % and 17 mol % *f*AGE content)	[64]
Comb like block copolymer + ethoxylated fluoroalkyl side chains	 amphiphilic surface	Contrast: Glass, PDMS (81 ± 5 %) removal of diatom Navicula High removal of Ulva and Navicula Settement and detachment strength of Ulva spores similar to PDMS	[65]
Polystyrene-b-hydrophobic fluorinated/hydrophilic PEG side chains		Navicula settement densities: ~750 cells/mm^2 Weakest Navicula detachment strength(hydrophilic PEGylated and glass surface) Robust Navicula detachment strength (hydrophobic fluorinated surface) Higher Ulva sporelings removal compared to PEGylated surface	[66]

Polystyrene + amphiphilic polyoxyethylene polytetrafluoroethylene side chains	 SnSzm copolymers	$\theta_w \geq 107°$, $\theta_h \geq 64°$ low surface tension: γ_S = 13-15 mJ/m^2 sligth ↑surface energy with ↓Sz unit content Ulva zoospores settlement density slightly lower than SEBS control Ulva zoospores biomass removal higher than SEBS control Adhesion srength of attached navicula cells: $S_{26}Sz_{23} > S_{81}Sz_{19}$ Percentage removal of attached navicula cells: $S_{26}Sz_{23\text{-}90} > S_{26}Sz_{23\text{-}100}$, $S_{81}Sz_{19\text{-}100} \approx S_{81}Sz_{19\text{-}90}$	[52]
Methacrylate copolymers + catechol + trifluoromethyl side chains	 poly(DMA-co-TFME-co-EG9ME)	T_g = 70-150 °C T_g = 142.4-74.2 °C (TFME content: 3-95 %) Excellent adhesion strength to metal and plastic substrate ↑contact angle with ↑TFME content Posess antifouling performance to some extent (43 % TFEM content)	[67]

to mimic the tributyltin-based antifouling paint except that tin-free matrix utilizes copper, silicon or zinc-based ester moieties to substitute tributyltin-ester group. Several Tin-free self-polishing coatings based on acrylic or methacrylic have been prepared *via* various methods [69]. Rong Yang's groups [70] fabricated the antifouling thin films of poly[N,N-dimethyl-N-metha-cryloxyethyl-](3-sulfopropyl)-co-2-(dimethyl-amino)ethyl methacrylate-co-ethylene glycol dimethacrylate] (PDDE). This all-dry-initiated chemical vapour deposition (iCVD) zwitter-ionic films exhibited a low advancing contact angles (~ 43°) and a receding contact angles (~ 20°). According to their fouling resistance studies, the iCVD zwitterionic surface exhibits a lower adsorbed bovine serum albumin (~ 14 ng/cm^2) and humic acid (HA)(~ 80 ng/cm^2) concentration to a control gold surface (~ 210 ng/cm^2 and ~ 120 ng/cm^2) as well as a control unreacted copolymer surface (~ 200 ng/cm^2 and ~ 130 ng/cm^2), which makes them able to be used for antifouling materials. Zhao *et al.* [71] synthesized a series of polymer brushes of poly-(2-hydroxyethyl methacrylate) (polyHEMA) and poly(hydroxypropyl methacrylate) (polyHPMA) with different film thickness and studied the effect on the antifouling performance. The film thickness was demonstrated to affect the antifouling performance, too thin or too thick polymer brushes lead to large protein adsorption. Surfaces with the appropriate film thickness of ~25-45 nm for polyHPMA and ~20-45 nm for polyHEMA can achieve almost zero protein adsorption (< 0.3 ng/cm^2) from single-protein solution and diluted human blood plasma and serum. Furthermore, bacteria *Cytophaga lytica* adhesion test demonstrated that polyHPMA and polyHEMA surface exhibited a very low bacteria adhesion (~ 0.38×10^5 and ~ 0.96×10^5 cells/cm^2). Introduction of polydodecafluoroheptyl methacrylate (DFHM) into the poly(2-hydroxyethyl methacrylate) antifouling membranes was prepared by Peng *et al.* [72]. The result suggested that the poly(HEMA/DFHM) membranes possess much better fouling resistance to proteins, higher permeation fluxes and better fouling release properties. Wang *et al.* [73] investigated various porous microstructure surfaces with controllable sizes based on silicone–acrylate copolymers (PSiA). They controlled the mean diameter and depth of the honeycomb microstructures surface (HMS) *via* changing the species, concentration of the organic amine and the silicon–acrylate mass ratio of copolymer. This HMS samples have a minimal Ulva spores density (65.8 ± 15.3 spores/mm^2) and Navicula subminuscula density (132.7 ± 17.1 spores/mm^2) as well as Stauroneis constrita density (281.8 ±34.6 spores/mm^2), which demonstrated that the zoospore settlement and diatom attachment were strongly influenced by the scale of micro-structures and organisms.

In recent years, degradable self-polishing antifouling materials have been proposed and investigated as alternative self-polishing antifouling polymers for conventional self-polishing polymers of tin-free antifouling paint [74,75]. Recently several studies explored the potential use of polycaprolactone (PCL) and polyurethane (PU) for minimizing adhesive biofouling. Polycaprolactone (PCL) has been utilized to diverse applications because of their good biocompatibility, biodegradability, nontoxicity and permeable properties, such as biomedical materials, packaging materials and antifouling coatings. Fay *et al.* [76] prepared copolymers of caprolactone with δ-valerolactone and L-lactide by ring-opening polymerization and further examined the kinetics of degradation and controlled release of bioactive molecules. The paper concluded that the incorporation of a comonomer such as L-lactide or δ-valerolactone led to a faster degradation than that of PCL homopolymer. Fay *et al.* [76] later synthesized biodegradable block copolymers composed of poly(ε-caprolactone) (PCL) and poly(sebacic acid) (PSA). They discussed the hydration-degradation-erosion process *via* analytical methods and found the polymer has the potential use as a binder for antimicrobial applications. But future works are needed to eliminate the high corrosion efficiency in water [77]. Degradable polyurethane antifouling materials have been reported in the literature for its excellent mechanical properties and low toxicity [78,79]. Xu and co-workers [80] demonstrated that polyurethane with poly(ε-caprolactone) (PCL) as the segments of the main chain and poly(triisopropylsilyl acrylate) (PTIPSA) as the side chains can hydrolyze and form a self-renewal surface in the seawater. In their studies, they found the degradation rate decreased with the PTIPSA content increased, in contrast, the hydrolysis rate increased with the PTIPSA content increased. They also found that as the PTIPSA content increases, the contact angle gradually increases due to the hydrophobic PTIPSA moieties covered on the surface increase. Additionally, as shown in Fig. 5, the number of barnacles grown on the polyurethane surface decreases as the PTIPSA content increases, indicating that the antibiofouling ability increases with the PTIPSA content which revealed that this polyurethane coating has good antifouling ability. Polyurethane with poly(ε-caprolactone) segment and N-(2,4,6-trichlorophenyl)maleimide (TCPM) pendant groups has been prepared. The TCPM pendant group content increased from 0 to 29.8 wt % leads to higher T_g and lower adhesive fouling organism [81]. It is known that polylactides (PLAs) posses the similar performance as polycaprolactone, we believe this material may also provide us an opportunity to further develop antifouling coatings with biodegradable, nontoxic and longer longevity properties [82].

Bio-inspired antifouling coatings and materials: Bionic antifouling coatings can be divided into two categories: natural product extract and synthetic materials. In marine environment, many large marine animals such as shark, dolphin and whale can exhibit an excellent anti-bioadhesive performance. The micro-nano structures of this biological surface provide biomimetic ways to constructing an environmentally friendly benign antibacterial paint. Techniques such as electrochemical techniques, optical and scanning electron microscopes and field trial can be utilized to measure the antifouling performance of natural product incorporation into an antifouling coating [83]. Cho *et al*. [84] established catecholic block copolymer architectures containing poly(methyl methacrylate) and polydopamine. The sharp reduction (by up to 50 %) in protein adsorption and thermal stability makes it attractive for antifouling coatings. Wan's group [85] prepared the Sylgard-184 silicone elastomer negative replica and resorcinol-formaldehyde (RF) positive replica by biomimicking the patterns of natural trifolium. The removal assay and settlement assay with two microalgae (Chlorella and Nannochloropsis maritima) was used to test their fouling-release and antifouling properties, respectively. The results indicate that the structure of microspines on Trifolium leaf can inhibit settlement of microalgae and facilitate the cell release. Polyaspartamide derivatives con-taining poly(ethylene glycol) and catechol pendant groups has great potential for use in adhesive coating for antifouling surface [86]. Kuang and Messersmith [87] synthesized high-density antifouling poly(sulfobetaine methacrylate) (pSBMA) brushes. The bifunctional tripeptide bromide (BrYKY)/pSBMA modification significantly reduced bacterial and mammalian cell adhesion and showed a long-term performance, which opened an avenue for combating fouling.

Recently, bioinspried polydopamine (PDA) antifouling and antimicrobial materials have drawn great attention. Jiang *et al*. [88] studied the hydrophobic polypropylene (PP) porous membrane with bioinspired polydopamine (PDA) and poly(N-vinyl pyrrolidone) (PVP) layers. The introduction of PDA and PVP layers significantly improved the hydrophilicity and wettability of the membranes. Furthermore, the modified membranes showed remarkable antimicrobial activity and

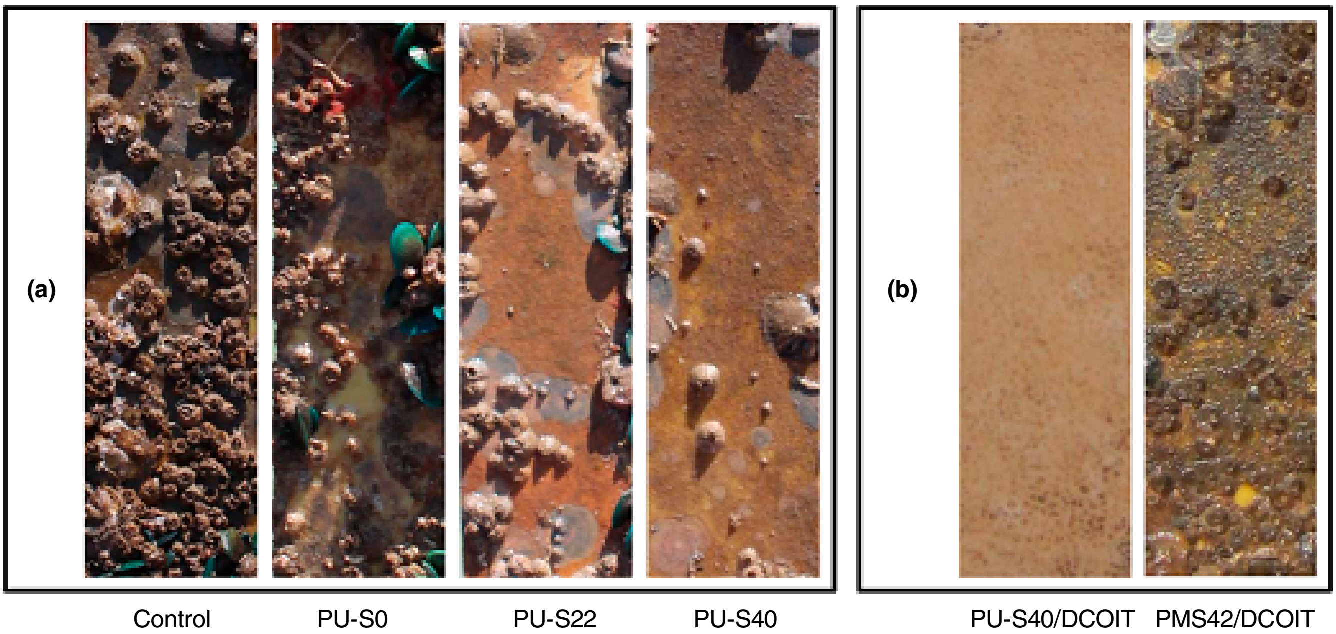


Fig. 5. Typical images of tested panels: (a) panels coated with PU-Sx; (b) panels coated with PU-S40 and PMS-42 in combination with DCOIT (10 wt %) after immersion in seawater for 3 months [Ref. 79]

satisfying long-term stability and durability. Polyethersulfone (PES) ultrafiltration membrane with a thin PDA layer and fluorinated polyamine formed low free energy microdomains to impede the coalescence of foulants and lower the adhesion force between foulants and the membrane [89], which provided the membrane surface with prominent fouling-release property with the minimal value of total flux decline ratio was ~8.9 % and the flux recovery ratio reached 98.6 %. The contact angle of fluorinated PDA/PES composite membrane increased from 43.5° to 87.0° by incorporation of fluorinated polyamine due to the hydrophobic nature of grafted perfluoroalkyl groups. The surface free energy decreased from 56.5 mJ/m^2 for the PDA/PES composite membrane to 27.4 mJ/m^2 for the fluorinated PDA/PES membrane. Adhesive dopamine molecule conjugated with zwitterionic sulfobetaine moiety (SB-DA) pH-Modulated thin films was investigated by Huang *et al.* [90]. This film provides the best resistance to nonspecific adsorption due to the high coverage and stability of the SB-DA films.

Incorporation of bioactive compounds derived from marine organisms in antifouling coatings is another promising approach to minimize the accumulation of marine fouling. Pérez and co-workers [91] assayed the antifouling activity of celastroids, quinone-methide nortriterpenes isolated from *Maytenus vitis-idaea* and *Maytenus spinosa*. They found tingenone and celastrol were the most effective inhibitors of the settlement of fouling organisms, which provide a more environmentally friendly alternative for the control of biofouling, replacing toxic additives actually in use in marine paints. Shao *et al.* [92] investigated the resorcylic acid lactones from the gorgonian-derived fungus *Cochliobolus lunatus*, which showed a significant effect on larval settlement. They examined the antibacterial and cytotoxic activities of these compounds as well as the larval settlement of barnacle *Balanus amphitrite*. In the existing literatures, barettin (cyclo[(6-bromo-8- entryptophan)arginine]), isolated as a Z/E mixture and 8,9-dihydrobarettin (cyclo[(6-bromotryptophan)arginine]), isolated from the marine sponge Geodia barrette with ability to inhibit the settlement of cyprid larvae of the barnacle *Balanus improvisus* was studied by Martin Sjogren's group [93]. They suggested that the compounds produced by the sponge can be efficient against larval settlement and fouling growth.

Up to now, bio-inspried and synthetic materials with antifouling properties were considered as novel environmentally benign and economically viable technologies for the purpose of preventing unwanted accumulation of adhesion and protein adsorption at surfaces and interfaces. Despite this, though, the large-scale production of natural product extract with antifouling and antimicrobial performance is difficult to achieve because of the significant expense and limited natural resource, which makes it still in laboratory phase and difficult to be commercialized.

Other antifouling materials: Several other substances have been utilized to reduce the adhesive befouling such as, PEG-based antifouling coatings [65,94], antifouling ultrafiltration membranes [95], nanomaterials [96-98], sol-gel coating [99,100], peptidomimetic polymer [101,102].

In the late 1980s, researchers found that poly(ethylene glycol) (PEG) moieties strongly resist protein adsorption. This has stimulated tremendous interest in the development of PEG-based antifouling technologies to control fouling. Immobilization of antibacterial peptide and magainin I as well as anti-adhesive PEG on a titanium oxide surface was established by Peyre *et al.* [103]. This materials not only considerably reduced the adhension of both proteins and bacteria but also inhibited the growth of remaining adhered bacteria. Cross-linked hyperbranched fluoropolymer (HBFP) and poly(ethylene glycol) (PEG) amphiphilic networks coating with PEG weight percentages of 14, 29, 45 and 55 % exhibited lower contact angles of water and increase in the surface energy with increase in the hydrophilic PEG composition. This material also provided better antifouling performance than did a standard poly-(dimethylsiloxane) elastomer (PDMSE) coating [104]. The grafting of PEG molecules on $SiCl_4$-plasma functionalized polyamide (PA) and polyester (PET) surface has been reported by Dong *et al.* [105]. The PEG-grafted polyamide and PET surfaces significantly inhibited biofilm formation by *L. monocytogenes* compared with the corresponding unmodified substrates [105]. Four-armed PEG-dopamine coatings synthesized by Mizrahi *et al.* [106] provided excellent resistance against proteins and cells for extended durations as well as long-lasting anti-fouling performance. However, this kind of antifouling materials are limited by the low polymer densities and relatively thin coating, further works should be made for enhancing its antimicrobial properties. Antifouling membranes largely attract considerable practical and theoretical research, which resulted in the emergence of numerous synthetic pathways. Park *et al.* [107] introduced silver nanoparticles (AgNPs) onto poly(vinylidene fluoride) (PVDF) membrane to develop sustainable anti-biofouling ultrafiltration membrane nanocomposites. The Ag-PVDF membrane nanocomposite significantly inhibits the growth of bacteria on the membrane surface. Additionally, the AgNPs are not released from the membrane surface because of the robust covalent bond between the AgNPs and the thiolated PVDF membrane. Xu *et al.* [108] synthesized grapheme oxide-based filtration membranes with photocatalytic antifouling function, this membrane possess favourable photocatalytic antifouling function under UV light irradiation, which can be used in water purification. Sun's group used silica-poly(vinyl pyrrolidone) (PVP) nanocomposite as a hydrophilic additive to modify polyethersulfone (PES) membranes for the purpose of enhancing the antifouling property, they suggested that the PES membrane with a silica-PVP nanocomposite additive has lower membrane fouling. Moreover, the foulings adhered on this membrane can be easily removed [109].

A number of nanostructured materials have been demonstrated to possess antimicrobial performance such as, silver nanoparticles, graphene (G) and graphene oxide (GO), zinc oxide, copper, TiO_2. Since silver nanoparticles have been proved to have strong bactericidal abilities, antimicrobial films containing silver ions or nanoparticles have been generated by various methods. The PDA-based AgNPs coatings were produced by Ren *et al.* [110]. The fouling-resistant behaviour of these AgNP-modified surface was tested *via* a marine microalga *Dunaliella tertiolecta* and a freshwater green alga community, they found that these AgNP coatings decreased the adhesion of microalgae by above 85 % in both seawater and freshwater environments. In addition, the AgNP coatings didn't influence the viability of microalgae cells, which provide a facile method to prepared low-toxic surface. Yin *et al*. [111] coupled with silver nanoparticles possess antibacterial performance and long-term effectiveness. They found that the nanosilver-containing super hydrophobic coatings can efficiently prevent the adhesion of sulfate-reducing bacteria (SRB). However, they also demonstrated that the generation of a sustained flux of Ag^+ ions reduced bacterial adhesion but resulted in damaging the bacterial cells [112]. Graphene and graphene oxide was also found to have antibacterial properties. Wang *et al*. [113] anchored ZnO nanoparticles onto GO sheet for imparting superior antibacterial properties and tested the antibacterial activity and cytotoxicity of the ZnO/GO composites. Thin-film composite polyamide membranes functionalized with graphene oxide decreased the extent of bacterial growth on membranes [114].

Antifouling materials preparation methods: A wide range of antifouling materials has resulted in a variety of preparation methods such as free radical polymerization [115], emulsion polymerization [38], condensation polymerization reaction [40], graft copolymerization [116], block copolymerization [66], photochemical cross-linking (UV-cured) [47]. Living free radical polymerization has been widely used in various applications owing to its mild reaction conditions and effectiveness in controlling molecular weight and polydispersity, Lejars *et al.* [42] synthesized TBDMSiMA- and PDMSMA-based graft copolymers *via* reversible addition radical polymerization process, the polymers obtained a narrow monomodal distribution which was contronlled between 1.07-1.13. In addition, Zhang's group [117] grafted poly(sulfobetaine methacrylate) (polySBMA) brushes onto glass surface by using atom transfer radical polymerization (ATRP), only few spores attached on polySBMA surface compared with glass surface and 66 % spores removed by 63 kPa impact pressure.

Conclusion

Antifouling coatings were developed to prevent the colonization of biofouling on submerged surface. Two main coatings are used for antifouling application: fouling-released coatings which minimize the adhesive strength of fouling settlement with a low surface energy and modulus; tin-free degradable coating coupled with biocide provide a smooth surface to prevent the fouling adhesion. Meanwhile, bio-inspired coatings with micro-nano structure surface and other nanoparticles with antimicrobial performance are also applied to marine antifouling, however, the significant expense and limited natural resource as well as biological incompatibility has hindered its large-scale use, respectively. While considerable progress has been made in the design of antifouling technologies, ongoing research in this area should be made for the development of antifouling materials with durable antibacterial in the future. Non-toxic paints with high antifouling efficiency have drawn much interest of researchers and scientists. Tin-free self-polishing antifouling coatings and low-surface-energy antifouling paints gradually become the promising environmentally benign and economically viable antifouling coatings.

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