

## Novel hybrid anti-biofouling coatings with a self-peeling and self-generated micro-structured soft and dynamic surface

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We prepared hybrid antifouling coatings with a self-generated topographical microgel surface by mixing small surface-functionalized microgels with a self-peeling resin and a poly-functional cross-linking agent (axiridine). The microgels were prepared by copolymerizing acrylamide (AAm) and methacrylic acid (MAA). The resin is a random terpolymer made of methyl methacrylate (MMA), acrylic acid (AA) and triisopropylsilyl methacrylate (TIPSM). During the coating process, the microgels and terpolymer chains are cross-linked together to form a hard thin film. After it is immersed into sea water, the microgels dispersed and embedded on the film surface are swollen, generating small and soft bumps, and at the same time, the hydrolysis of TIPSM makes the surface layer hydrophilic, forming a thin layer of soft hydrogel. A combination of these two effects leads to a soft and dynamic topographical surface layer with many well-structured microgel bumps. Such a soft and dynamic surface is self-generating; namely, the hydrolysis of TIPSM eventually makes the terpolymer chains on the surface soluble so that a thin layer of them is gradually dissolved and washed away and the inner layer is further exposed to sea water. Here, both the self-peeling and topographically structured surface by small microgel bumps lead to antifouling properties. To test such a novel idea, we prepared a set of coatings with different microgel and TIPSM contents and evaluated their antifouling properties in a real marine environment. We found some optimal composition at which the coatings showed excellent antifouling properties in the field tests. Moreover, adding the microgels reduces the amount of expensive TIPSM required so that the coatings become more cost-effective, which is vitally important for industrial applications.

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### Introduction

Biofouling, an undesirable accumulation of microorganisms, plants, and marine animals, on wetted material surfaces, including ships, sea-farming devices and power-plant cooling tubes, is a widespread problem.<sup>1</sup> The biofouling typically starts with the development of a microbial thin layer of bacteria, diatoms (unicellular algae) and their extracellular products.<sup>2,3</sup> This fouling layer will subsequently and effectively lead to gradual settlement and growth of macro-foulers, including barnacles, tubeworms and macro-algae. The biofouling makes the ship's surface rough, which increases the fuel consumption, bio-corrosion, and dry-docking cleaning frequency, and also leads to speed loss and the potential invasion of alien aquatic

species.<sup>4-7</sup> In order to prevent or reduce these effects, anti-fouling coatings have to be used. Toxic antifouling paints containing copper and other biocides are widely used nowadays, providing effective control over many biofouling species. Due to increasing environmental concern, more non-toxic approaches have been designed and studied to control biofouling.

Recently, hydrogels (cross-linked polymer networks swollen in water) as a soft, wet and dynamic layer have been studied as potential biocide-free and environmentally benign antifouling materials. Freeman *et al.*<sup>8</sup> showed that cross-linked poly(ethylene glycol) diacrylate hydrogels exhibited lower protein adsorption. Katsuyama *et al.*<sup>9</sup> found that acidic hydrogels made of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) and poly(acrylic acid) (PAA), especially those made of PAA, effectively inhibit the germination of the zoospores originating from *Laminaria angustata*. Murosaki *et al.*<sup>10,11</sup> and Rasmussen *et al.*<sup>12,13</sup> revealed the slow settlement of cultured *Balanus amphitrite* cyprid larvae on various hydrogel surfaces. Recently, we also reported a novel kind of self-hydrogel-generating anti-fouling coating made of cross-linked copolymer chains containing methacrylate (MMA), acrylic acid (AA) and hydrolysable tributylsilyl methacrylate (TBSM). These coatings have sufficient

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mechanical strength and appropriate antifouling ability towards barnacles in a real marine environment.<sup>14</sup> However, the problem is that TBSM is an expensive monomer.

On the other hand, creating a microtopographic surface on elastomeric materials is a novel alternative and nontoxic strategy to inhibit the settlement (initial attachment) of fouling organisms. Various previous studies have showed that a properly structured surface could play an effective role in slowing down the settlement of marine species on submerged surfaces. For example, Brennan *et al.*<sup>15–21</sup> showed that their topographic surfaces, including Sharklet AF, can effectively reduce marine biofouling and the attachment of zoospores of *Ulva* by 86% in comparison with a smooth PDMS surface in their laboratory tests. de Nys *et al.*<sup>22–25</sup> demonstrated that some micro-textured surfaces could also reduce the attachment of diatoms and other biofouling. These studies have mainly revealed that the biofouling of different marine organisms is closely related to different surface topographies (patterns). Therefore, it would be difficult to use one surface topography to prevent a range of marine organisms that exist in the real and complicated marine environment, not to mention that it is difficult, if not impossible, and expensive to pattern a ship's surface. In reality, the development of effective anti-biofouling involves a range of considerations, *e.g.*, how to avoid or repair the damage of a static micro-structured coating surface in the marine environment remains a real challenge. Up to now, most previous studies of the influence of surface patterns are on PDMS, just proof of concept, not on real ship-coating materials.

A literature search shows that there have mainly been four different approaches for designing and developing anti-marine-biofouling coatings; namely, using (1) hydrolysable layer-by-layer self-polishing or self-peeling polymers; (2) soft/dynamic surfaces (hydrogels); (3) microscopically structured topographic (patterned) surfaces, and (4) slow controlled release of non-natural or natural toxic agents. In principle, it is relatively easy to composite toxic agents into a given existing coating material. In the current study, we developed a novel idea of combining the first three approaches together to form a self-renewing and self-peeling microscopically structured topographical hydrogel surface by mixing small microgels into a hydrolysable terpolymer resin together with a polyfunctional cross-linking agent. In such a design, those microgels embedded on the water-contacting surface (the top layer) swell first, resulting in a patterned surface

with many small half-spherical soft/dynamic bumps whose inter-distance can be properly controlled by the number of microgels dispersed inside the coating; at the same time, the slow hydrolysis of the top layer leads to the formation of a brush-like soft/dynamic layer between those swollen microgel bumps. Note that it is those cross-linked bonds that keep the swollen microgels on the coating surface. Further hydrolysis of the top layer breaks the cross-linked bonds and makes the terpolymer chains more hydrophilic. After a sufficient number of cross-linked bonds are broken, the hydrolyzed terpolymer chains, together with the microgels, are gradually dissolved into sea water and washed away. In such a way, the next layer of microgels and hydrolysable resins are exposed to sea water so that the swelling and hydrolyzing processes continue (self-renewal) to prevent/reduce the settlement and biofouling of marine animals on such a coating surface. On the other hand, the hydrophobic resin beneath the surface layer provides an adhesion force and required mechanical properties, as schematically shown in Fig. 1. In the current study, we mainly proved our concept of novel coatings and elucidated how their antifouling ability is related to the microgel properties, the coating composition, the hydrolysis/degradation rate, and the surface microtopography.

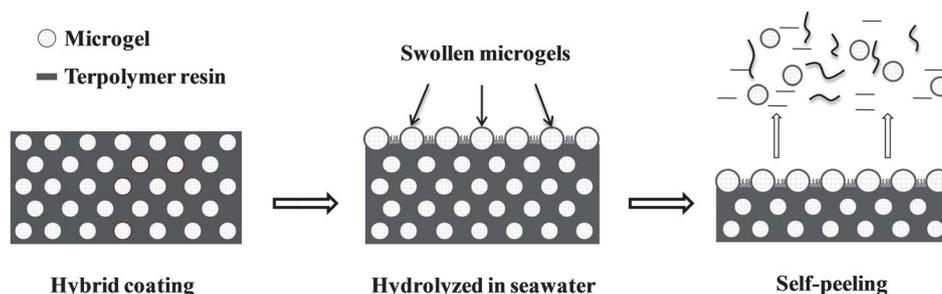
## Experimental

### Reagents

Xylene, *n*-butyl acetate, *n*-butanol, methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), acrylamide (AAM), methacrylic acid (MAA), azobisisobutyronitrile (AIBN) and *N,N'*-methylene-bis-acrylamide (BIS) were purchased from Alfa Co. Polyfunctional axiridine cross-linking agent (XAMA 7) and triisopropylsilyl methacrylate (TIPSM) were kindly provided by Bayer Co., and Yuki Gosei Kogyo Co., respectively. AIBN and AAM was re-crystallized three times in acetone. MAA was further purified by distillation under reduced pressure to remove the inhibitor. Artificial seawater (ASW) was prepared according to D1141-98.<sup>26</sup> Other reagents were used as received without further purification.

### Synthesis of PMMA-*co*-BA-*co*-AA dispersion agent

A random terpolymer made of MMA, BA and AA was first synthesized and used as a dispersion agent for the microgel preparation. The synthesis of the terpolymer is outlined as follows. A mixed solvent, xylene and *n*-butanol (7 : 3 v/v) was



**Fig. 1** Schematic of a novel hybrid coating made of a hydrolysable polymer resin (grey) and small microgels (white spheres), which can automatically form a soft, micro-structured, self-peeling and dynamic anti-biofouling surface after its immersion in seawater.

purged with nitrogen gas for 30 min before it was heated to 110 °C, and then a solution mixture of MMA (35.5 g), BA (27.1 g), AA (4.0 g) and initiator AIBN (0.4 g) was added into the solvent mixture using a syringe pump with a feeding rate of 0.28 mL min<sup>-1</sup>. After all the monomers were added, the reaction was allowed to proceed for another 4 h at 110 °C. Note that the choice of such a solvent mixture is mainly because we have to simultaneously dissolve the resin and disperse the microgels in a common medium so that we can use the existing coating protocol currently used in the shipyard.

### Preparation of PAAM-co-MAA microgels

The dispersion with a high solid content of narrow-size distributed PAAM-co-MAA microgels was prepared in *n*-butanol via a two-step dispersion polymerization process. First, AAM monomer (1.0 g), MAA (0.5 g), BIS (0.008 g) and the terpolymer dispersing agent (3.8 g) were mixed in 40.0 g *n*-butanol. The solution mixture was purged with nitrogen gas for 30 min and then heated to 70 °C before AIBN (0.03 g) dissolved in *n*-butanol (1.0 mL) was added to initiate the polymerization. After reaction for ~2 h, a solution mixture of AAM (12.4 g), MAA (6.2 g), BIS (0.09 g), the terpolymer dispersing agent (13.5 g) and AIBN (0.04) in *n*-butanol (25.5 g) was slowly fed into the reaction mixture at a rate of 0.12 mL min<sup>-1</sup> by a syringe pump. After all the monomers were added, the reaction continued for another 8 h at 70 °C. Such prepared microgels have many functional -COOH groups on their surfaces. The choice of *n*-butanol was due to its compatibility with xylene so that the microgel dispersion can be directly mixed with the resin without any further treatment. Note that using the terpolymer as the dispersing agent also improves compatibility with the resin.

The solid content of the microgels in the dispersion was gravimetrically determined by the following procedure. (1) 10 mL of the dispersion was centrifuged for 20 min at 10<sup>4</sup> rpm; (2) the supernatant was removed; (3) the concentrated microgels were re-dispersed in 10 mL *n*-butanol; (4) steps 2 and 3 were repeated three times to remove the remaining monomers, and (5) the resultant concentrated microgel dispersion was dried under vacuum until its weight became constant. The extent of monomer conversion (MC) was calculated according to  $MC = W_p/W_o \times 100\%$ , where  $W_o$  and  $W_p$  are the weights of initial monomers and final microgels, respectively. The size distribution of the microgel was measured by dynamic laser light scattering (LLS) (Zetasizer, the Brookhaven Instruments).

### Synthesis of PMMA-co-TIPSM-co-AA terpolymer resin

The poly(methyl methacrylate-co-triisopropylsilyl methacrylate-co-acrylic acid) random terpolymer resins were synthesized by free radical polymerization as follows. The solvent, xylene or a mixture of xylene and *n*-butyl acetate, in a 5-necked flask equipped with an agitator, a reflux condenser, a thermometer and a dropping funnel was purged by nitrogen and then heated to 90 °C before a mixture of nitrogen-purged monomers (MMA, TIPSM and AA) and initiator was added dropwise at constant speed over a period of 4 h. The polymerization continued for another 4 h at 90 °C. The molar masses of such obtained

copolymers are in the range 1.4 to 3.0 × 10<sup>4</sup> g mol<sup>-1</sup>. Table 1 summarizes the chemical compositions of different reactive mixtures used for the synthesis of different copolymer resins.

### Coating preparation

Table 2 lists the compositions of all the coatings used in the current study, where the coating M-00-T1 was prepared using a solution of copolymer T1 with XAMA 7 added as a cross-linking agent. The mixture was kept at room temperature for 30 min to allow the copolymer chains to be partially cross-linked. The 30 min standing time was designed for real shipyard application because it takes a certain time to mix and load the spray-coating device. The other coatings were prepared by first mixing each copolymer solution with an appropriate amount of the microgel dispersion and then adding XAMA 7 as a cross-linking agent. Each of such mixtures was also reacted at room temperature for 30 min. For the degradation, swelling and SEM experiments, each coating was first made on a glass slide using a film applicator so that its thickness was kept at ~300 μm, then dried at 25 °C for 2 days, and finally further dried at 80 °C for one more day.

### Coating characterization

To measure the self-peeling and the swelling rates, each dried coating, together with its glass substrate, was weighed ( $W_o$ ) before dipping into a tank of artificial sea water (ASW) which was renewed every two days. After different immersion time periods the glass slides were taken out and immersed in distilled water for 5 min before its surface was gently dried with a tissue and its weight was recorded ( $W_{t,wet}$ ). In parallel, some of the immersed coatings were dried at 25 °C for one day and then at 100 °C for 6 h before their weights ( $W_{t,dry}$ ) were recorded. The weight difference between  $W_{t,wet}$  and  $W_o$  reflects the swelling (water-adsorption) of each coating, while the weight difference between  $W_o$  and  $W_{t,dry}$  shows the weight-loss (self-polishing or -peeling) of each coating, which can be further converted to the thickness change ( $\Delta_{thickness}$ ) for a given density and coating area. For each resin, three coated glass slides were prepared and measured. Therefore, each result reported and used hereafter was averaged over three identical coatings.

The microgels were also imaged by using a scanning electron microscope (SEM, Hitachi S-3400) at an acceleration voltage of 15 kV. For the SEM characterization, each sample was prepared by adding a drop of the *n*-butanol-diluted microgel dispersion onto a carbon-coated copper grid and drying at room temperature. To characterize the time-dependent morphology of the immersed coatings, each glass slide was taken out of the ASW at

**Table 1** Chemical compositions used to prepare different terpolymer resins, where the initiator AIBN was kept at 0.8 g and the reaction temperature was 90 °C

Terpolymer resin	T1	T2	T3	T4
Xylene/g	90.0	90.0	90.0	90.0
<i>n</i> -Butyl acetate/g	10.0	10.0	10.0	10.0
MMA/g	57.2	62.2	67.2	72.2
TIPSM/g	41.0	36.0	31.0	26.0
AA/g	1.8	1.8	1.8	1.8

**Table 2** Compositions of hybrid coatings made of hydrolysable terpolymer resins and small microgels, where coatings were prepared at 25.0 °C and poly-functional axiridine (4.3 wt%) was used as a cross-linking agent

Coating	Microgel/wt%	Terpolymer	
		Type	Content/wt%
M-00-T1	0	T1	100.0
M-10-T1	10.0	T1	90.0
M-20-T1	20.0	T1	80.0
M-30-T1	30.0	T1	70.0
M-40-T1	40.0	T1	60.0
M-30-T2	30.0	T2	70.0
M-30-T3	30.0	T3	70.0
M-30-T4	30.0	T4	70.0

different time intervals and immersed in distilled water for 5 min before it was further freeze-dried for 24 h.

### Biofouling tests

The biofouling tests of the coating in shallow submergence strictly follow the GB 5370-2007 procedure. Namely, each epoxy panel ( $300 \times 200 \times 3 \text{ mm}^3$ ) was rubbed with sandpaper. Each coating on such a panel was prepared using a paintbrush. The resultant coating has a thickness of  $\sim 600 \mu\text{m}$ . Such prepared coatings were first dried at 25 °C for two days and then at 80 °C for one more day. For each type of coating, three identical panels were prepared and attached to a frame so that they could be submerged at different depths in the range 0.2–2.0 m from a stationary experimental raft positioned in a sheltered bay with water currents ( $< 2 \text{ m s}^{-1}$ ) at Xiamen, China ( $24^\circ 45' \text{ N}$ ,  $118^\circ 07' \text{ E}$ ), on Aug 15, 2012. After immersion for a certain time period, these panels were taken out of the sea and gently washed with seawater. After photographing, they were immediately returned to their original places in the sea to continue the biofouling test.

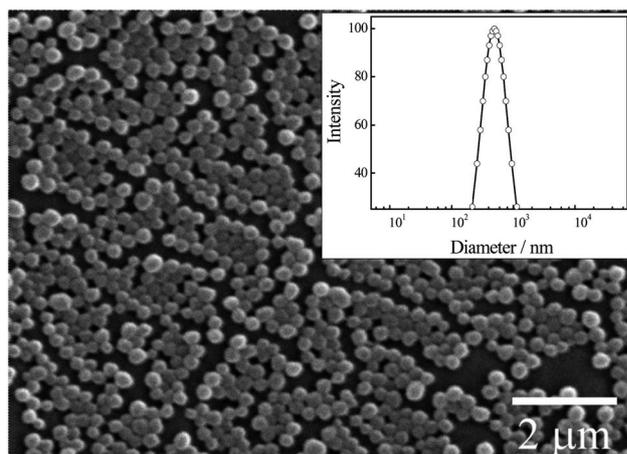
## Results and discussion

### Characterization of PAAM-co-MAA microgels

Fig. 2 shows the SEM image of the PAAM-co-MAA microgels synthesized in *n*-butanol, where their estimated average radius is in the range 390–450 nm, smaller than the average hydrodynamic diameter ( $\sim 494 \text{ nm}$ ) obtained from dynamic LLS (the inset on Fig. 2), which is reasonable because (1) the microgels measured by dynamic LLS were swollen in *n*-butanol, and (2) the average hydrodynamic size measured in dynamic LLS is intensity weighted, while the average diameter from the SEM image is number weighted. Both the SEM and dynamic LLS results reveal that such prepared microgels with many reactive –COOH groups on their periphery are narrowly distributed in size. In the current study, the microgel dispersion had a solid content of 19.1 wt%. Note that such a high solid content is one of the necessary conditions in compositing our novel self-peeling and surface-microstructured hybrid coatings.

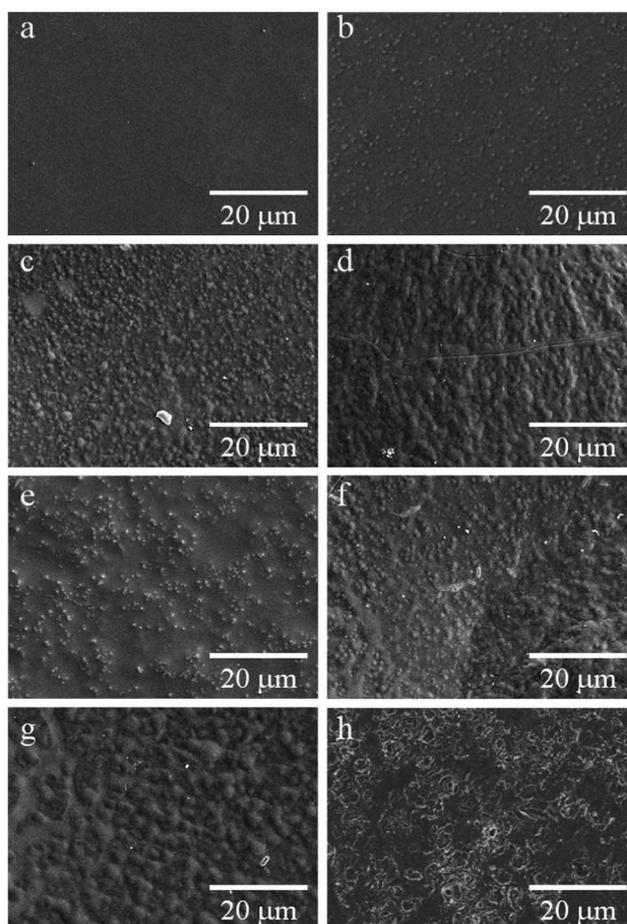
### Morphology studies of hybrid coatings

Fig. 3(a–d) shows that the coating has a smooth surface before immersion in ASW. After immersion in ASW for 2 days, the



**Fig. 2** SEM image of PAAM-MAA microgels, where the inset shows their hydrodynamic radius distribution in *n*-butanol solution at 25 °C.

microgels started to swell and bump out from the surface to form a micro-structured topography. Further immersion of such a coating in ASW resulted in a well-structured soft/



**Fig. 3** (a) SEM image of surface of coating M-30-T1 before immersion in ASW; (b–d) SEM images of surface of coating M-30-T1 after immersion in ASW for 2, 8 and 16 days, respectively; (e and f) SEM images of bottom layer of coating M-30-T1 and its surface after re-immersion in ASW for 8 days, and (g and h) surfaces of coatings M-30-T3 and M-00-T1, respectively, after immersion in ASW for 16 days.

dynamic hydrogel surface. After 16 days, a ridge-like surface was formed and the inter-distance between individual ridges became smaller. Fig. 3(e) shows that after peeling the soft hydrogel-like structured surface layer, the microgels and terpolymer chains underneath remain intact, even after immersion in ASW for 16 days, which is exactly what we want in our novel design. Fig. 3(f) shows that after re-immersion in ASW for 8 days, the layer underneath forms a similar topography surface again. A comparison of the coatings M-00-T1 and M-30-T3, where M-\*\* and T\* respectively denote the weight percentage of the microgel and the type of terpolymer used, shows that without the addition of the microgels that act as multi-functional cross-linking agents, many small holes were formed on the surface after its immersion in ASW for 16 days, presumably due to the washing away of the hydrolyzed fragments of the cross-linked terpolymer chains.<sup>14</sup> On the other hand, coatings M-30-T1 and M-30-T3 have similar surface topographies after their immersion in ASW for 16 days, indicating that the terpolymer composition has less effect on the resultant surface micro-structure.

### Swelling and degradation studies

Fig. 4 shows that as expected all the hybrid coatings swell in ASW and the swelling extent increases with the immersion time but slows down after half a month, indicating the gradual hydrolysis process of the triisopropyl ester bond in TIPSM. Also, as expected, the hybridization of the hydrophilic microgels into the terpolymer resin increases the water content and the thickness of the top hydrogel layer so that the relative swelling increases with the microgel content for a given immersion time. Note that coating M-00-T1 with no added microgel swells little because the hydrolysis of the TIPSM in the terpolymer is fairly slow so that water can slightly penetrate the coating surface to form a very thin layer of hydrogel.

As shown in Fig. 5, after immersion in ASW for two days, all the coatings tested start to lose weight. In comparison with coating M-00-T1 made of pure terpolymer resin T1 with no microgels, hybrid coatings generally lose their weight faster,

indicating a higher self-peeling rate. This is because in the swelling of the embedded hydrophilic microgels leads to more water in the hybrid coating and promotes the hydrolysis of the TIPSM inside the terpolymer resin, which makes those terpolymer chains on the top layer soluble so that they are washed away at a faster rate. This is why the self-peeling rate increases with the microgel content. It is also important to note that in our design, the degradation products released into seawater are mainly fragmented poly(methyl methacrylate) with some anionic carboxylate groups and triisopropylsilyl cation and PAMM-MAA copolymer chains. To the best of our knowledge, they are not harmful and nontoxic in marine environments. The degradation (weight loss) speed in the coating is mainly controlled by both the contents of TIPSM and microgel. We are able to regulate the self-peeling rate by adjusting the TIPSM/microgel ratio. For example, we can reduce the TIPSM content but increase the microgel content to compensate for the decrease of peeling rate, which practically enables us to use less expensive TIPSM monomer to reduce the cost. Furthermore, we investigated the effect of the hydrolysable TIPSM content on the self-peeling rate of the hybrid coatings in ASW for a fixed microgel content (30 wt%); *i.e.*, coatings M-30-T1, M-30-T2, M-30-T3 and M-30-T4, as shown in Table 2.

Fig. 6 reveals that for a given immersion time the relative weight loss of the hybrid coatings increases with the TIPSM content and the self-peeling rate (the slope) also increases with the TIPSM content. This is expected because adding more TIPSM comonomers to the terpolymer resin increases the hydrolysis rate so that the formation of a hydrogel layer on the coating surface becomes quicker. The adsorption of water further promotes the hydrolysis of the terpolymer chains underneath. The whole process becomes a self-accelerating one. Eventually, the top layer of the hybrid coating becomes so hydrophilic that the terpolymer chains inside dissolve in ASW and are washed away.

On the other hand, Fig. 7 shows a gradual weight gain after the hybrid coatings are immersed in ASW. Initially, the coatings

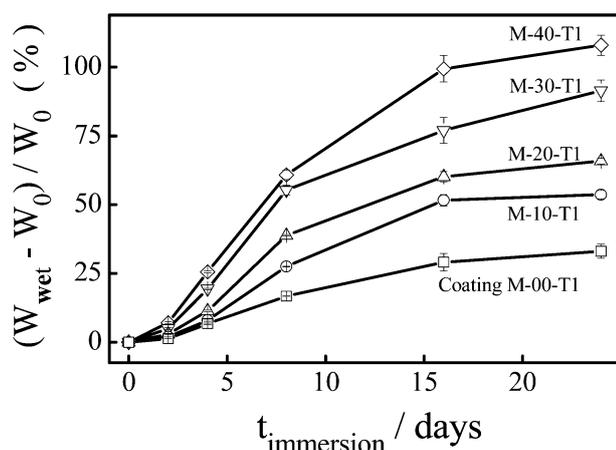


Fig. 4 Immersion-time dependence of the relative swelling of hybrid coatings with different microgel contents, as listed in Table 2, in ASW.

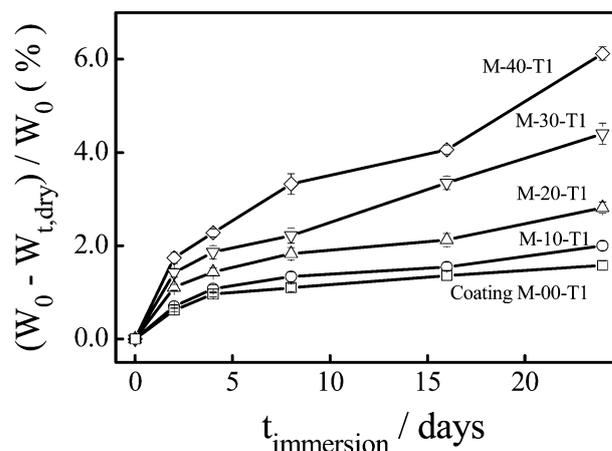


Fig. 5 Immersion-time dependence of relative weight loss of five coatings with different microgel contents in ASW, where each coating was prepared on a glass slide with dimensions of  $25.4 \times 76.2 \text{ mm}^2$ .

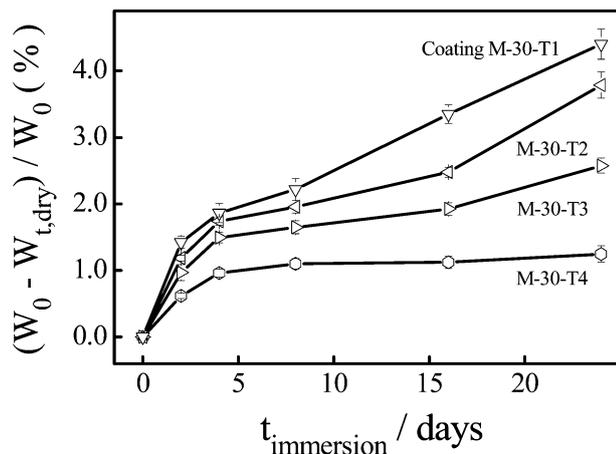


Fig. 6 Immersion-time dependence of relative weight loss of hybrid coatings with different terpolymer resins in ASW.

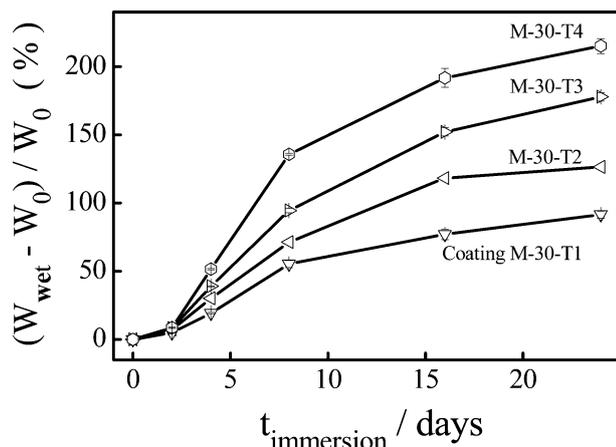


Fig. 7 Immersion-time dependence of relative swelling of hybrid coatings with different terpolymer resins in ASW, where each coating was prepared on a glass slide (25.4 × 76.2 mm<sup>2</sup>).

with different terpolymer contents behave similarly, indicating that at this stage (~2 days), water is mainly absorbed by the embedded microgels on the coating surface and the hydrolysis of TIPSM in the terpolymer resins is slower. Eight days after the immersion, the weight gain (the adsorption of water) of the hybrid coatings clearly increases with the TIPSM content, agreeing well with the self-peeling results in Fig. 6. Namely, the coating with a lower self-peeling rate keeps the top swollen hydrogel layer on the coating surface longer so that water is not able to further reach the microgels and terpolymer resins underneath, maintaining the mechanic strength of the coating.

### Antifouling properties

The settlement of most marine fouling organisms occurs within a time period as short as a few hours when they find a suitable substrate. For example, barnacles are one of the most familiar and typical organisms in marine biofouling. Their settlement on a submerged surface can be summarized as follows:<sup>27–29</sup> (1)

they start their life as *nauplius* larvae that feed on plankton. After undergoing a series of moults, a *nauplius* larvae transforms to a larval stage called *cypris* larvae or “cyprids” whose length is *ca.* 120–500 μm; (2) cyprids swim around in seawater and explore a suitable hard substrate surface for their settlement so that they can “walk” over it using a pair of attachment organs or “antennules” that secrete a temporary adhesive, which only takes 1–3 h; (3) a firmly attached juvenile further metamorphoses into a calcified adult barnacle to complete its transition to adult life, and (4) finally adult barnacles secrete “cement” within a couple of days and strongly settle themselves on the surface. As shown in Fig. 4–7, our coatings dramatically change their surface morphology to form a dynamic, soft and self-peeling thin layer within a few days, which helps to prevent the settlement of fouling organisms.

Fig. 8 shows that in comparison with the control (a blank epoxy panel), the number of barnacles grown on the hybrid coatings dramatically decreases when the microgel content is higher than 20 wt%, which can be surely attributed to the formation of a layer of the swollen hydrogel on the coating surface because previous results showed that a soft/dynamic and self-polishing hydrophilic surface can effectively prevent the initial protein adsorption and later sea animal biofouling by its hydration layer.<sup>30–33</sup> It was also claimed that there is a connection between the biofouling degree and the retention/release rate of water molecules from a surface. Murosaki *et al.*<sup>11</sup> showed that hydrophilic surfaces were not favorable for the settlement of a cyprid larvae of barnacles. A comparison of coating M-00-T1 with no added microgel and the other four hybrid coatings with different microgel contents leads us to strongly believe that the micro-structure generated by those small swollen microgel bumps also helps to reduce the biofouling, which might have a similar effect to shark skin patterns<sup>19,20,34</sup> or mollusk shells.<sup>35</sup>

It should be stated that even though many studies showed the anti-fouling potential of different topographical surfaces in terms of the attachment of barnacles,<sup>19,36</sup> algae,<sup>37,38</sup> and

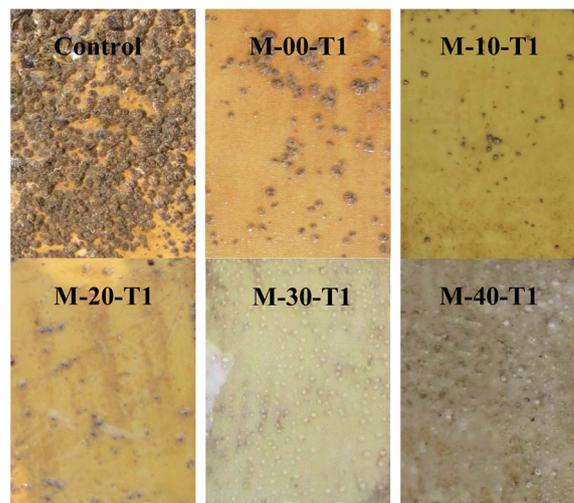


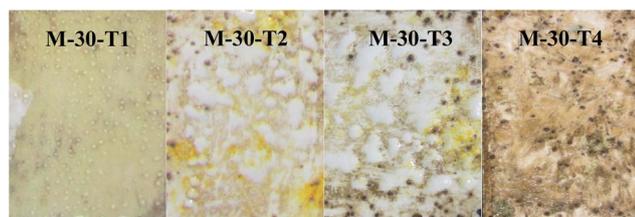
Fig. 8 Photographs of hybrid coatings with different microgel contents after field-testing in a real environment, where they were submerged 1.30–1.65 m under seawater for two months.

bacteria<sup>39,40</sup> in the marine environment, the underlying mechanism for these observations (*i.e.*, the settlement and attachment) still remains unclear. Brennan *et al.*<sup>19,20</sup> suggested that the settlement of barnacle *cypris* larvae is related to the size of topographical features; namely, it should be smaller than either the dimensions of the marine organisms at their settling stage or those parts of the larvae. On the other hand, de Nys *et al.*<sup>24,41</sup> proposed that the adhesion is related to the number of attachment points of a marine organism on the surface. In our current novel design, the slow self-peeling process self-renews the micro-structured surface in a layer-by-layer fashion. Note that coatings M-10-T1 and M-20-T1 with relatively lower microgel content were not able to effectively form a desired micro-topographic surface so that their anti-biofouling ability is relatively lower. On the other hand, coating M-40-T1 with a higher microgel content (40 wt%) shows excellent antifouling ability in the field test, but it became too soft with no mechanical strength after immersion in sea water so that it is impractical to use it in real applications. Therefore, it is critically important to choose an appropriate microgel content.

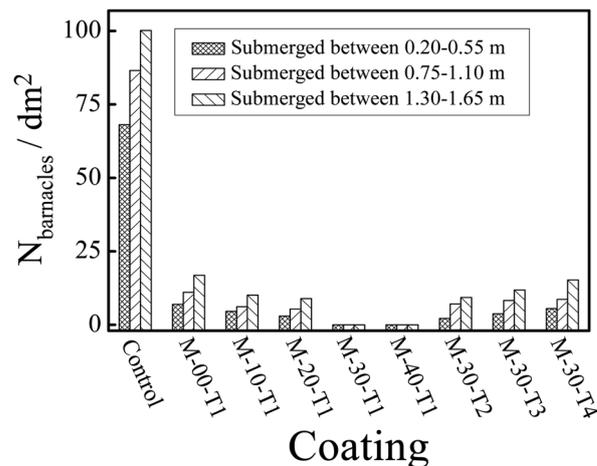
A comparison of coatings M-30-T1 and M-00-T1 shows that incorporating 30 wt% PAMM-MAA microgel beads generates a desired topography on the coating surface after it is immersed in seawater and results in better antifouling properties. Meanwhile, the self-peeling regenerates and retains such a micro-structured surface so that it resists the damage due to the deposition of various microorganisms in the sea. It shows that a combination of three different approaches leads to better antifouling properties.

Fig. 9 shows that the coatings with higher TIPSM contents in the terpolymer resin generally have better anti-barnacle performance. A comparison of coatings M-30-T1, M-30-T2, M-30-T3 and M-30-T4 reveals that here the self-peeling rate plays an important role in their antifouling performance. The real marine environment is more complicated because organics can gradually accumulate on the coating surface, constantly altering the surface's characteristics. It is expected that a micro-structured surface without an appropriate self-renewal rate can be easily damaged over a short period of time. Therefore, a self-renewing micro-topographic surface is vitally important for an anti-biofouling coating to have long-term good performance in a real sea environment.

Fig. 10 quantitatively summarizes the field-test results of different hybrid coatings. It is clear that for a given hybrid coating, more barnacles grew on it when it was immersed



**Fig. 9** Photographs of hybrid coatings with different terpolymer resins but an identical resin/microgel ratio (70 : 30, w/w), where all of them were submerged 1.30–1.65 m under seawater for two months.



**Fig. 10** Average density of barnacle *Balanus albicostatus* on different hybrid coatings after they were immersed in seawater at different depths for two months, where the control is an epoxy panel without any coating.

deeper into the sea between 1.30 and 1.65 m, which is generally true for any coating. The more important thing is that Fig. 10 tells us that the hybrid coatings with an appropriate amount of microgels, which result in a micro-structured coating surface after immersion in sea water, and a sufficiently higher TIPSM content in the terpolymer resin, which leads to a required self-polishing rate, generally have good anti-biofouling performance. On the other hand, for a given microgel content, the anti-biofouling ability of the hybrid coating decreases as the TIPSM content in the terpolymer resin decreases even though a similar micro-structure is formed on its surface, which clearly indicates that the micro-topographic surface alone is not able to effectively prevent biofouling in real sea water. On the other hand, the self-peeling alone also does not provide good anti-biofouling properties (*e.g.*, coating M-00-T1). Therefore, a combination of a properly micro-structured surface and a suitable self-peeling rate is one of the necessary conditions for the development of good anti-biofouling coatings.

## Conclusions

A new kind of antifouling hybrid coating has been successfully developed by mixing hydrolysable and cross-linkable terpolymer resins made of poly(methyl methacrylate-*co*-triisopropylsilyl methacrylate-*co*-acrylic acid) and small microgels made of poly(acrylamide-*co*-methacrylic acid), wherein the –COOH groups on the terpolymer chains and microgels can be cross-linked by a polyfunctional agent (axiridine). Our concept-proving experimental results have shown that (1) the swelling of small embedded and covalently attached microgels after the hybrid coating is immersed in sea water can cost-effectively generate a micro-structured surface with many sub-micrometer-sized soft bumps, and (2) the hydrolysis of the terpolymer chains can slowly lead to the formation of a thin and self-peeling layer of hydrogel on the surface. Our field tests in a real marine environment reveal that neither one of these two properties alone led to a satisfactory anti-biofouling coating,

but a combination of them results in a self-generating and self-peeling micro-structured soft and dynamic surface that could effectively prevent the settlement of barnacles. Moreover, the hybridization of small microgels in the terpolymer resins also reduces the expensive hydrolysable triisopropylsilyl methacrylate content and lowers the cost of the final coating, which is vitally important in real applications.

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