

Effects of hydrolyzable comonomer and cross-linking on anti-biofouling terpolymer coatings

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ABSTRACT

Antifouling coatings based on the cross-linked terpolymer chains made of methyl methacrylate (MMA), the hydrolyzable tributylsilyl methacrylate (TBSM) or triisopropylsilyl methacrylate (TIPSM) and acrylic acid (AA) were developed. By varying the hydrolyzable monomer content and the cross-linking degree, a set of such prepared coatings were evaluated in terms of their degradation rate, swelling degree, contact angle and antifouling properties. After immersed in seawater, such coatings quickly self-generate a thin and swollen hydrogel layer at the water-contacting surface due to the hydrolysis of the hydrolyzable groups on the surface. Further hydrolysis leads to a gradual degradation and self-peeling of this hydrogel layer. Their antifouling properties were evaluated by both the adsorption of fluorescence-labeled bovine serum albumin and the field-testing in a real marine environment. Our results reveal that it is such a layer-by-layer hydrogel formation and self-peeling process that leads to an excellent antifouling property. Therefore, it is vitally important to delicately balance the hydrogel formation and the self-peeling rate to achieve the best antifouling of such a coating by carefully choosing a proper cross-linking degree and a suitable content and type of the hydrolyzable comonomer.

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1. Introduction

The surface submerged into water (either a marine or fresh-water environment) will normally lead to the quick adhesion of some biological macromolecules, such as proteins, polysaccharides, and proteoglycans, within a few minutes. Further, such an adhered surface is gradually colonized by some living species, such as bacteria, single-cell diatoms, protozoa and rotifer, to form a film of biological species, typically within a few days. This fouling layer made of adhered microbes will subsequently and effectively leads to the settlement and growth of macro-foulers, including barnacles, tubeworms and macro-algae [1,2]. The marine biofouling is a serious economic and environment worldwide-problem. Just for an example, the surface roughness generated by the settlement of those macro-foulers increases the drag resistance and higher fuel

consumption, which could be as higher as 40% more. To remove this biofouling layer means more frequent dry-docking of a ship. In addition, the biofouling also lead to bio-corrosion and invasion of alien aquatic species because ships are constantly traveling around the world nowadays [2,3]. To solve such a big problem, different antifouling strategies and paints have been developed in the past.

Among those applicable antifouling paints, tributyltin (TBT) acrylate esters remain as one type of the most useful, effective and popular antifouling paints. However, this kind of paints has been banned worldwide since 2008 because of their high adverse effects on marine environment. Subsequently, copper and zinc have been chosen as substitutes for tin. However, a debate on the environmental impact of copper has also arisen [4], leading to a restricted usage of copper in the Baltic Sea. The intensive research in this area has resulted in lots of environmentally benign strategies to control and reduce biofouling, including generating anti-fouling agents from natural resources [5–8], using polymeric elastomers with a low surface energy [9–11], creating different surface topographies [12–15], utilizing various surface chemistry [16–19] and enzymes [20,21], applying a pulsed electrical field [22]. However, one has to note that some of these strategies look nice in publications but actually useless in real applications because they are either very expensive or impractical or both.

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Previous studies have revealed that a soft, wet and dynamic surface can effectively reduce the biofouling, such as hydrogels that have attracted more attention as potentially useful biocide-free alternatives and environmentally benign antifouling coatings. Jiang et al. [23,24] demonstrated that such hydrophilic materials, especially hydrolyzable zwitterionic polymers and their derivatives are good in antifouling. Ekblad et al. [25] showed that poly(ethylene glycol)-containing hydrogel is very effective in slowing down the settlement and promoting the antifouling. Katsuyama et al. [26] found that acidic hydrogels of PAMPS and PAA, especially PAA, inhibit the germination of the zoospores originating from *Laminaria angustata*. Murosaki et al. [27,28] and Rasmussen et al. [29,30] revealed that a slow settlement of cultured balanus amphitrite cyprid larvae on various hydrogel surfaces. These are just some proofs of the concept. However, such a soft surface can be easily destroyed by an external force in real applications. The adhesion of such a hydrophilic hydrogel layer onto a ship surface is another problem. Therefore, it is rather difficult, if not impossible, to apply them in shipyard. Recently, our group reported a novel kind of coatings for antifouling by using a copolymers containing tributylsilyl methacrylate (TBSM) that can be hydrolyzed in seawater to form a hydrogel on its water-contacting surface. Such coatings have a sufficient mechanical strength and antifouling ability to the barnacle when it was tested in real marine environment [31].

However, TBSM is an expensive monomer. In some patents literature [32–34], this hydrolyzable monomer was used with biocide for giving the coating a self-polishing property, normally; the hydrolyzable comonomer content is kept more than 50 wt%. In our earlier research, TBSM copolymers were used to design a self-generating hydrogel for antifouling coating, the coating shows a reliable antifouling performance until the TBSM content was increased to 48.2 wt% [31]. How to reduce its content but still keep the hydrogel-generating property is the problem that we like to address in the current study. Our idea is to prepare the “self-generating hydrogel” surface by introducing polyfunctional axiridine (XAMA 7) as a cross-linking agent besides using different hydrolyzable monomers. In such an approach, a set of resins copolymers made of different ratios of methyl methacrylate (MMA), acrylic acid (AA) and triisopropylsilyl or tributylsilyl methacrylate (TIPSM or TBSM) were first synthesized using free radical copolymerization. Each resin was then fully mixed with the cross-linking agent in an equal stoichiometric ratio before coating on a surface. By varying the type and content of hydrolyzable monomer and the amount of the cross-linking agent, we prepared and evaluated a set of coatings in terms of their surface hydrophilicity, swelling and degradation rates, their ability of resisting protein adsorption, and their anti-biofouling property of barnacles in real marine environment. Our main objective is how to use the cross-linking to reduce the expensive hydrolyzable monomer content and maintain a proper self-peeling rate.

2. Experimental

2.1. Reagents

Xylene, *n*-butyl acetate, methyl methacrylate (MMA), acrylic acid (AA), azobisisobutyronitrile (AIBN) were purchased from Alfa Co. LTD. Tributylsilyl methacrylate (TBSM) and triisopropylsilyl methacrylate (TIPSM) were kindly provided by Yuki Gosei Kogyo Co., LTD. Polyfunctional axiridine (XAMA 7) as a cross-linking agent to react with –COOH group on acrylic acid was a gift from Bayer Co., LTD. The initiator, AIBN, was re-crystallized three times from acetone before used. Artificial seawater (ASW) was prepared according to D1141-98 [35]. Other reagents were used as received without further purification.

2.2. Synthesis of copolymer

The terpolymers were synthesized by free radical polymerization in a mixture solvent of xylene and *n*-butyl acetate by solution polymerization. The solvent was heated to 90 °C under nitrogen and then a mixture of nitrogen-purged monomers and initiator was added dropwise into the solvent mixture at a constant speed over a period of 4 h. After that, the polymerization continued for another 4 h at 90 °C. The molar masses of resultant copolymers were controlled in the range $(1.3–3.1) \times 10^4$ g/mol to maintain their viscoelastic properties. The chemical compositions of different reactive mixtures used in this study are listed in Table 1.

2.3. Coating procedure

The coatings with AA monomer (terpolymers 3–10) were prepared by mixing each corresponding solution and XAMA 7 with an equal stoichiometric ratio at the room temperature for ~30 min before it was painted on a surface. Scheme 1 schematically shows the resin synthesis and the coating formation procedure. In the degradation, swelling, contact angle and ATR-FTIR measurements, each coating was applied on a glass slide with a film applicator and the film thickness was controlled ~300 μm. Coatings 3–10 were dried at 25 °C for 2 days then at 80 °C for one day. Coatings 1 and 2 were dried at 25 °C for one week to ensure a complete removal of solvent, where the high temperature was avoided because of possible cross-linking reaction even without any added cross-linking agent.

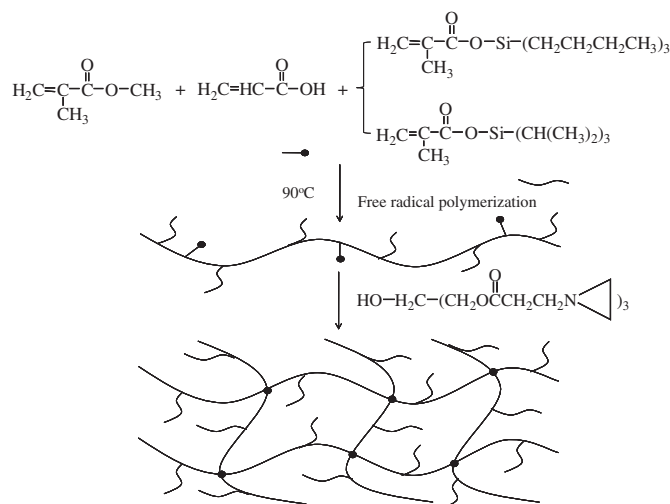
2.4. Swelling and degradation evaluation

To in-situ monitor the degradation and swelling of each coating, the gravimetric method was used; namely, each glass slide used was weighted before and after the coating to determine the dry weight (W_0) of the coated thin film. Three slides of each coating were used to get an average value and deviation. Each coated glass slide was weighted after different times immersed in a tank of ASW that was renewed every other day. After taking the slide out of ASW, we immersed it in distilled water for 5 min and then gently dried it before its weight ($W_{t,wet}$) was recorded. In parallel, some of these glass slides after immersed for different times were dried at 25 °C for one day and then at 100 °C for 6 h before their weights ($W_{t,dry}$) were recorded. This procedure was repeated on day 2, 4, 8, 16, and 24. The weight difference between $W_{t,wet}$ and W_0 reflects the swelling of each coating. On the other hand, the weight difference between W_0 and $W_{t,dry}$ shows the degradation (self-peeling) of each coating, which can be converted to the thickness change ($\Delta_{thickness}$) for a given density and coating size.

Table 1

Compositions of resins prepared by free radical copolymerization with 0.7 mol% of AIBN as initiator at 90.0 °C.

Resin	Xylene/g	<i>n</i> -butyl acetate/g	MMA/g	TBSM/g (mol)	TIPSM/g (mol)	AA/g
1	100.0	–	51.8	48.2 (0.17)	–	–
2	100.0	–	51.8	–	41.1 (0.17)	–
3	90.0	10.0	50.0	48.2 (0.17)	–	1.8
4	90.0	10.0	50.0	–	41.1 (0.17)	1.8
5	90.0	10.0	53.0	–	38.1	1.8
6	90.0	10.0	57.0	–	34.1	1.8
7	90.0	10.0	61.0	–	30.1	1.8
8	90.0	10.0	50.0	–	41.1	0.9
9	90.0	10.0	50.0	–	41.1	2.7
10	90.0	10.0	50.0	–	41.1	3.6



Scheme 1. Schematic of resin synthesis and coating formation process.

2.5. Contact angle goniometry and ATR-FTIR

After immersed in ASW for different times, each slide was taken out, immersed in distilled water for 5 min, and dried at the room temperature for 2 days before the contact angle and ATR-FTIR measurements. Static contact angle measurements were performed on a Powereach JC2000C Optical Contact Angle Meter as follows. One little drop of MilliQ water was formed on the tip of a micro-pipettor by controlling a manual liquid dispenser. After the glass slide on a raising platform contacted the drop, it was lowered to detach the drop from the micro-pipette. After the droplet reaches its steady state, we took its image and determined the corresponding contact angle. Five different points on each sample were tested, photographed and measured to obtain an average value. The infrared spectra were recorded by a Nicolet 8700 FTIR Spectrometer.

2.6. Protein adsorption test

Each coating was first immersed in ASW for 8 days and then washed by distilled water. After such a treatment, the slide was immersed in a 0.1 mg/mL solution of FITC-BSA in 0.1 M phosphate buffer at pH 7.4 for 48 h. The amount of protein bounded was evaluated by the fluorescence intensity using an Olympus FV-1000 confocal microscope. Protein releasing test was conducted by first rinsing the coating with 20 mL of PBS and then measuring the decrease in the fluorescence intensity immediately.

2.7. Biofouling measurements

The field test in shallow submergence follows the GB 5370-2007 procedure. Each epoxy panel ($300 \times 200 \times 3 \text{ mm}^3$) was first rubbed with a sandpaper and then coated with a paintbrush to form a thin film of $\sim 500 \mu\text{m}$ in thickness. Choosing the epoxy panel was due to its suitable mechanical strength against sea wave and the corrosion resistant. Each coating was dried at $25 \text{ }^\circ\text{C}$ for 2 days and then at $80 \text{ }^\circ\text{C}$ for one more day. For each type of coating, three identical panels were prepared and attached one above another to a frame so that they were submerged in different depths in the range 0.2–2.0 m from a stationary experimental raft that was positioned in a sheltered bay with weak water currents (less than 2 m/s) at Xiamen, China ($24^\circ 45' \text{N}$, $118^\circ 07' \text{E}$), on June 23, 2011. From time to time, those testing panels were taken out of the sea and gently

washed with seawater, photographed and immediately re-immersed into their original places to continue the antifouling test. We used the number of barnacles settled on each panel to quantify the biofouling because barnacles are main macro-foulers on our panels.

3. Result and discussion

Fig. 1 shows the degradation kinetics of Coating 1 and 2 in seawater. Note that these two coatings have an identical molar content of hydrolyzable monomer and with no cross-linking. The initial quick weight loss is presumably due to the release of low molar mass components, such as residual solvents and un-reacted monomers [36]. After the initial weight loss, the decrease of the coating thickness reaches a stable rate after 2 days, indicating the self-polishing process. Coating 2 degrades slower than Coating 1, which is attributed to the fact that TIPSM has a larger triisopropyl side group than TBSM, i.e., the effect of stereo-hindrance.

As shown in Fig. 2, Coatings 3–6 have a smaller initial weight loss than Coating 2 because these coatings were cross-linked and prepared at a higher temperature ($80 \text{ }^\circ\text{C}$). After two days, the weight loss rate of Coating 2 becomes stable. Coatings 3–6 have a slower overall weight loss rate than Coating 2. Note that the initial hydrolysis only leads to the swelling of the top layer of each coating to form a hydrogel, not the dissolution in ASW when the terpolymer chains are cross-linked together. Fig. 2 also shows that after immersed in ASW for a long time, the coating with a higher TIPSM content loses its weight faster. This is because the hydrogel formed at the interface with more hydrolyzable TIPSM has a tendency to be gradually broken into small soluble copolymer chains or clusters so that they are washed away. In comparison, Coating 3 lost more weight than Coating 4 after a long immersion period, which is due to that fact that TBSM has a higher hydrolysis rate than TIPSM.

Fig. 3 shows the swelling properties of Coating 2–7. $W_{t,wet}$ gradually increases with the immersion time, presumably because continuous hydrolysis of triisopropyl ester bond increases the thickness and water absorption of the hydrogel layer. As expected, more triisopropyl ester groups result in more anionic carboxylate groups after the hydrolysis so that the top thin hydrogel layer becomes more hydrophilic and swells more with higher water content, which leads to $W_{t,wet}$ increases with the TIPSM content for a given immersion time period. Note that in the initial period, after 4 days, $W_{t,wet}$ of the Coating 3 increases more than Coating 4,

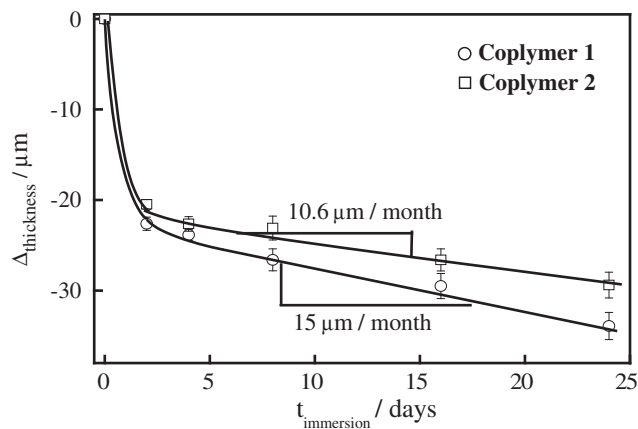


Fig. 1. Immersion-time dependence of coating thickness change in ASW, where $\Delta_{\text{thickness}}$ is defined as $W_{t,dry} - W_0$.

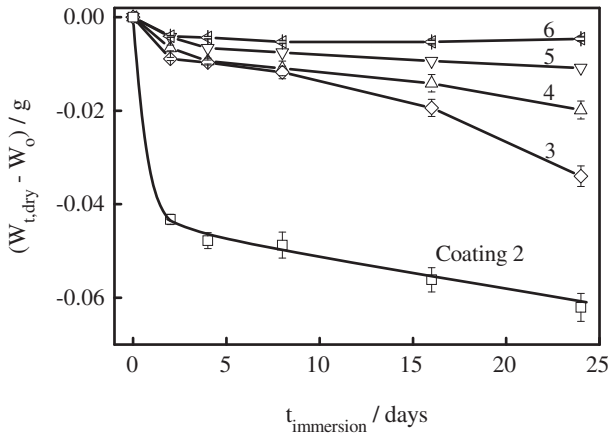


Fig. 2. Immersion-time dependence of relative weight loss of coatings with different hydrolyzable monomer contents in ASW, where squares: TIPSM coating with no cross-linking; and others symbols: Coating with cross-linking, and each coating was prepared on a glass slide with a dimension of 25.4 × 76.2 mm².

containing the same molar mass of TIPSM, indicating the higher hydrolysis speed of TBSM leads to a more rapidly formed hydrogel layer on the coating surface. In a long immersion period, Coating 4 swelled much more than Coating 3. Comparing the results of the degradation, we can conclude there is a competition between swelling and degradation: Coating 4 made from TIPSM copolymer with the lower degradation caused by the lower hydrolysis speed can maintain more water on the coating surface than Coating 3 made from TBSM copolymer, the lower degradation speed of Coating 4 can “hold” the hydrogel on the coating surface for a longer time. For Coating 2, without cross-linking, the coating swells very little and $W_{t,wet}$ decreases in the long immersion period because those sufficiently hydrolyzed chains with no cross-linking dissolved in seawater.

The contact angle was used to monitor the change in surface hydrophilicity after each coating was immersed in ASW for different time periods. Fig. 4 reveals that as expected, Coatings 1–8 are hydrophobic with a contact angle higher than 90° before they are immersed into ASW. After immersed in ASW for 4 days, their contact angle gradually decreases and finally reaches a stable corresponding value. It is clear that increasing the TIPSM content results in a smaller final contact angle (Coatings 4–7) because the hydrolysis of more triisopropyl ester groups leads to more anionic

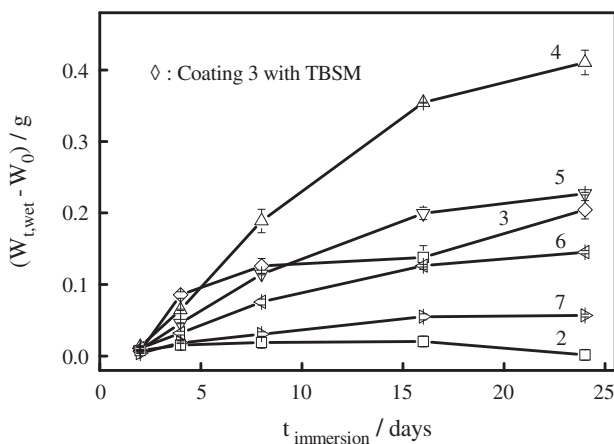


Fig. 3. Immersion-time dependence of swelling of coatings prepared with different resins, as listed in Table 1, in ASW.

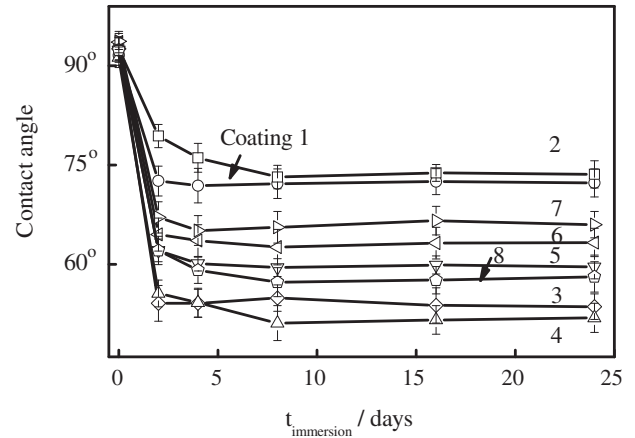


Fig. 4. Immersion-time dependence of contact angle of coatings prepared with different resins, as listed in Table 1, in ASW.

carboxylate groups so that the thin hydrogel surface layer is more hydrophilic. In comparison, Coatings 1 and 2 with no cross-linking have a higher contact angle because they lack the ability to form a hydrogel layer on the water-contacting surface. Instead, the hydrolyzed chains are simply dissolved into seawater, while for those cross-linked coatings, polymer chains inside the top hydrogel layer can be more hydrolyzed without being washed away because of the cross-linking. This also explains that Coating 8 with less cross-linking has a higher contact angle than Coating 4 with an identical TIPSM content. A comparison of its degradation and swelling results shows that there is no formation of a complete hydrogel layer on the surface of Coating 8 because there is no sufficient cross-linking, presumably only leading to branched chains/clusters.

The above results from the contact angle measurements are supported by the ATR-FTIR study, as shown in Fig. 5. Namely, after the coatings were immersed for 2 days, a new peak at ~1550 cm⁻¹ belonged to the asymmetrical stretching vibration of carboxylic anion clearly appears and its intensity increases with the immersion time, indicating that more carboxylic anions are generated on the coating surface after its immersion in ASW. A comparison of Coatings 2 and 4 shows that more carboxylic anions are generated on the surface of the cross-linked Coating 4.

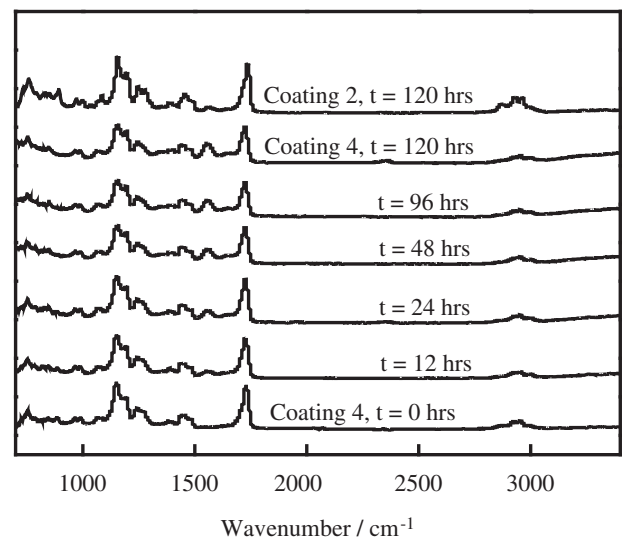


Fig. 5. ATR-FTIR spectra of coating surface of Coatings 2 and 4 before and after immersed in ASW for different immersion times.

Further, we investigated the cross-linking effect on the coating degradation in ASW for a fixed amount of hydrolyzable TIPS_M comonomer; namely, Coatings 4, 8–10. Fig. 6 reveals that even only two days after their immersion in ASW, the coating prepared with a higher amount of cross-linking agent loses less amount of its weight, indicating a lower peeling (degradation) rate of the coating with a higher cross-linking degree. Actually, this is an expected result because when the polymer chains are more cross-linked together, they have a less chance to become completely detached from the gel network and soluble in seawater even if they are highly hydrolyzed with many carboxylic anionic groups on their chain backbones.

On the other hand, Fig. 7 shows an expected gradual weight increase after the coatings were immersed in ASW. Initially, Coating 4 swells faster than Coatings 9 and 10 because it has a lower cross-linking degree so that it hydrolyzes faster and absorbs more water. Eight days after the immersion, the swelling (water adsorption) increases with the cross-linking degree, agreeing with the degradation results in Fig. 6. Namely, the coating with a higher cross-linking degree peels off slower and absorbs more water. Due to an insufficient cross-linking degree, Coating 8 only slightly swells and most of the hydrolyzed chains are dissolved into seawater.

To evaluate the protein resistance, coatings were first immersed in ASW for 8 days and then in a solution of FITC-labeled BSA in PBS. The fluorescence intensity of each tested coating was compared, where we used a polystyrene surface as a control. Literature results suggested that a hydrophilic non-fouling surface could prevent the protein adsorption and biofouling by creating a strong hydrolyzed surface layer [37–40] and there exists a correlation between biofouling and those retained/released bound water molecules from a surface.

Fig. 8 shows that the adsorption of protein decreases as the TIPS_M content increases, while Coatings 4, 9 and 10 with a higher cross-linking degree have a better antifouling property than Coating 8. On the other hand, Coatings 1 and 2, with no cross-linking resist the protein adsorption poorly because there is no hydrogel layer formed on their surfaces, indicating that the self-peeling is important but only the self-peeling is not sufficient to prevent the protein adsorption. Namely, a sufficient amount of cross-linking can effectively prevent the leaching-out of highly hydrolyzed chains so that the swollen surface becomes more negatively charged with more entrapped/bound water molecules, making the adsorption of proteins on it more difficult.

Fig. 9 shows the field-tested results of Coatings 1–7. The Control is a blank epoxy panel and used as a reference. The number of

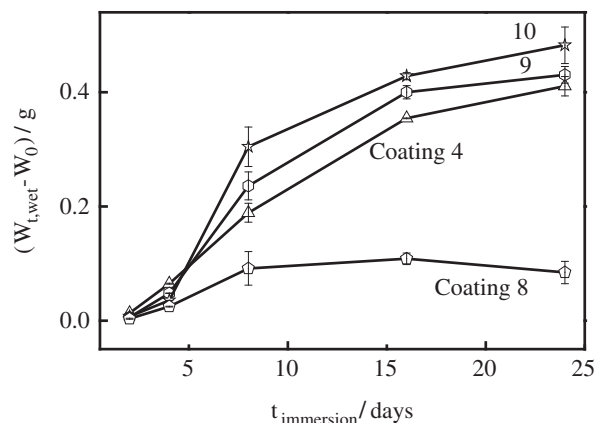


Fig. 7. Immersion-time dependence of swelling of coatings with different cross-linking degrees in ASW, where each coating was prepared on a glass slide ($25.4 \times 76.2 \text{ mm}^2$).

barnacles grew on these panels dramatically decreases when the copolymer chains inside the resin are cross-linked together to form a surface hydrogel that slowly undergoes the self-peeling in seawater. A comparison of Coating 4–7 reveals that for a given cross-linking degree, the antifouling ability clearly increases with the hydrolyzable TIPS_M content. However, there is a catch; namely, the higher the TIPS_M content, the softer the coating after it is immersed in seawater. For real applications, a delicate balance must be obtained. Fig. 9 also shows that for a fixed cross-linking degree, Coating 4 with TIPS_M provides a better antifouling property than Coating 3 with TBSM, presumably because it adsorbs more water. It is also interesting to note that the antifouling ability of Coating 2 is poorer than that of Coating 1 because here only the hydrolysis rate matters when the polymer chains are not cross-linked together.

Fig. 10 shows that the coatings with the cross-linked chains exhibit better antifouling ability than Coating 2 with no cross-linking. Agreeing well with our above “in-vitro” tests, Coating 8 with an insufficient cross-linking degree shows a poorer antifouling ability than its counterparts, revealing the formation of a good layer of hydrogel on the coating surface is important. On the other hand, Coating 10 with the highest cross-linking degree also shows a poorer antifouling property than Coatings 4 and 9. These results indicate that a proper self-peeling rate is also important. Therefore, there is a delicate balance between the formation of a hydrogel surface layer and the self-peeling rate of the hydrolyzed chains;

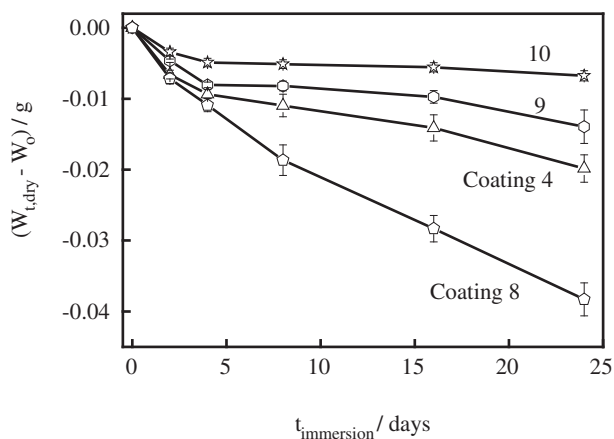


Fig. 6. Immersion-time dependence of weight loss of Coatings with different cross-linking degrees in ASW.

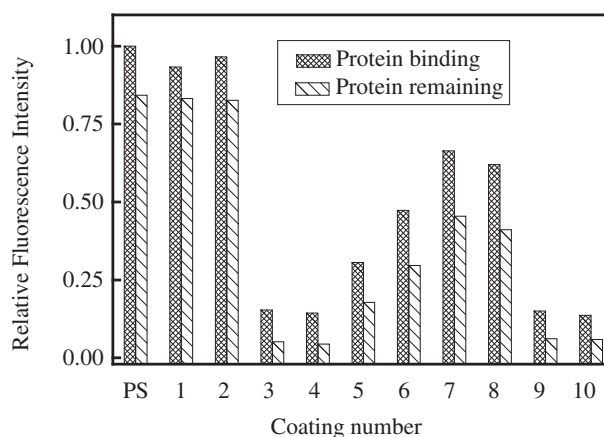


Fig. 8. Protein binding and release results from the different coatings using FITC-labeled BSA in a PBS solution.

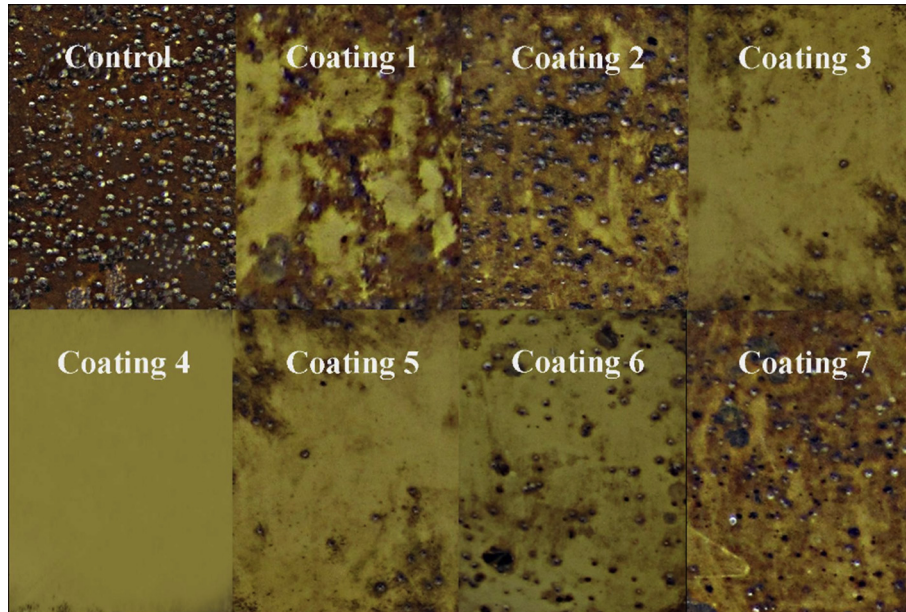


Fig. 9. Photographs of field-tested coatings with different amounts and types of hydrolyzable monomers, where all of them were submerged 1.30–1.65 m under seawater after two months.

namely, we have to carefully choose proper amounts of hydrolyzable monomer and cross-linking agent.

Fig. 11 summarizes the average surface density of barnacle *B. albicostatus* on all the field-tested panels after 2-month immersion in seawater at different depths. For a given coating, barnacles grow more when it is immersed deeper between 1.30 and 1.65 m. Quantitatively, Fig. 11 shows that with no cross-linking, individual polymer chains with sufficient hydrolysis leach out

and the self-peeling itself is not able to effectively prevent the fouling. On the other hand, the over-cross-linked chains can form a good, soft and dynamic hydrogel on the coating surface but it also significantly reduces the self-peeling rate so that it is important to balance these two effects. As shown in Fig. 11, the coatings with more hydrolyzable monomer and a suitable cross-linking degree can effectively prevent the settlement and growth of barnacle.

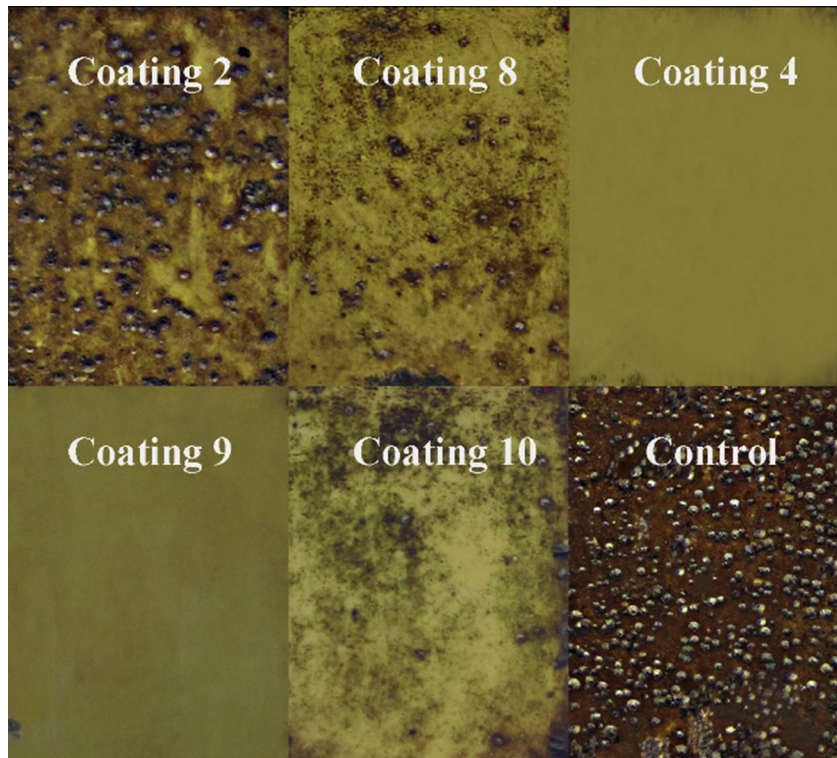


Fig. 10. Typical photographs of field-tested coatings with different cross-linking degrees, where all of them were submerged 1.30–1.65 m under seawater after two months.

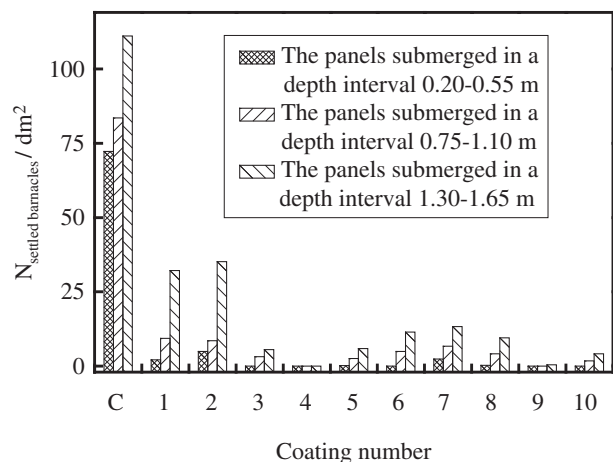


Fig. 11. Average surface density of barnacle *Balanus albicostatus* on field-tested coatings immersed in seawater at different depths after two months, where C is a control epoxy panel without coating.

4. Conclusion

Our current study of the effects of the type and amount of hydrolyzable comonomer (tributylsilyl methacrylate, TBSM, and triisopropylsilyl methacrylate, TIPSM) and the cross-linking degree on the antifouling properties of different coatings mainly made of poly(methyl methacrylate) (PMMA) reveals that 1) polyfunctional axiridine (XAMA 7) can effectively cross-link copolymer chains (poly(MMA-co-TBSM) or poly(MMA-co-TIPSN)) inside the coating; and 2) after such a coating is immersed into seawater, the hydrolysis of TBSM or TIPSM on the cross-linked copolymer chains leads to the formation of a thin hydrogel layer on the surface when a proper amount of XAMA 7 is used and a slow and gradual self-peeling of the coating surface while the underneath cross-linked chains still remain hydrophobic and provide a sufficient adhesive force and mechanical strength. It is this layer-by-layer hydrogel formation and self-peeling process on the surface that prevent the adsorption of protein and the growth of barnacle *B. albicostatus* on the coating. In general, 1) the TIPSM coatings exhibit a better antifouling property than the TBSM coatings; and 2) increasing the content of hydrolyzable comonomer inside a coating increases its antifouling ability, which is well correlated to its more hydrophilic and swollen surface and its lower contact angle. Our current results demonstrate that both the formation and the self-peeling of a thin hydrogel layer on the coating surface play important roles in its antifouling property. Therefore, there exists a delicate balance between the hydrogel formation and the self-peeling rates that can be properly adjusted by the type and content of hydrolyzable comonomer and the cross-linking degree. In the development of an applicable antifouling coating, one also needs to consider its cost, mechanical strength and surface-adhesion.

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