

Coatings with a self-generating hydrogel surface for antifouling

Laiyong Xie^{a,b,*}, Fei Hong^{a,b}, Chuanxin He^{a,b}, Chunfeng Ma^a, Jianhong Liu^b, Guangzhao Zhang^a, Chi Wu^{a,c}

^aThe Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

^bSchool of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen, Guangdong 518060, China

^cDepartment of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

ARTICLE INFO

Article history:

Received 10 March 2011

Received in revised form
12 June 2011

Accepted 19 June 2011

Available online 25 June 2011

Keywords:

Anti-biofouling coating

Self-generating hydrogel

Gel networks

ABSTRACT

We prepared a coating by mixing a polyfunctional axiridine cross-linking agent and a self-polishing resin pre-synthesized via the polymerization of methyl methacrylate (MMA), acrylic acid (AA) and tributylsilyl methacrylate (TBSM). The coating can be easily applied on a surface to form a cross-linked polymer film by conventional brushing or spraying method. After immersing it into seawater, the film self-generates a thin soft and dynamic layer of hydrogel at the water-contacting surface because of the hydrolysis of TBSM. Such a hydrogel-formation process continues after gradual corrosion and detachment of each top hydrophilic layer. This hydrogel-formation and self-peeling property makes it ideal in various antifouling applications. In the current study, besides the synthesis and preparation of this novel kind of coatings, we focused on the correlation between the TBSM content and the antifouling property by using contact angle, water-absorption, and antifouling measurements. The results of immersing different coatings in shallow submergence for two months reveal that the addition of more TBSM leads to a more hydrophilic surface and a better antifouling property.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The marine biofouling normally refers to some harmful and wasteful accumulation and rapid growth of marine living matters, especially in summer time, on material surfaces immersed under seawater. Such a biofouling process generally involves three stages as follows. 1) An initial accumulation of some organics adsorbed on the surface; 2) the surface is gradually colonized by some living matters, such as bacteria, single-cell diatoms, protozoa and rotifer, to form a thin film of biological species; and 3) finally macro-foulers, such as barnacles, tubeworms and macro-algae, settle and grow on the surface [1–3]. Biofouling can result in some devastating effects for various applications. For example, it can cause high frictional resistance leading to higher fuel consumption, up to 40% [4]. To remove them, a ship has to be more frequently dry-docked [5]. In a nuclear power plant, the biofouling of its cooling water discharge pipe can greatly reduce its efficiency. In addition, the biofouling can also lead to bio-corrosion and invasion of alien aquatic species [3].

In order to solve biofouling problems, different antifouling paints have been proposed, developed and applied. Among them, self-polishing antifouling coatings (SPC) are widely used nowadays. They normally contain a self-polishing resin, antifouling agents and other additives. Here, the self-polishing means that after immersed in seawater, soluble additives in the top layer of the coating gradually dissolve into seawater, allowing seawater to fill in and react with the hydrolyzable groups inside the resin under the slightly alkaline conditions so that the resin gradually transforms from hydrophobic to hydrophilic. As the transformation continues, individual polymer chains in the top layer become sufficiently hydrophilic and finally soluble into seawater and are washed away by the flow. In this way, the coating is gradually peeled away layer by layer in seawater. With a properly adjusted self-polishing property, such a coating can steadily release antifouling agents at a constant rate. Moreover, the self-polishing process also results in a smoother surface [3]. Previously, the tributyltin acrylate ester was the most useful and popular self-polishing resin. However, it has some high adverse effects on our marine environment so that it was gradually banned in manufacturing antifouling paints since 2003 [3]. Subsequently, copper, zinc and silyl acrylates are chosen as substitutes. However, some studies showed cuprous oxide used as biocide also potentially threat to our marine environment even if it is not as bad as tin [6,7]. In order to find a better replacement, many environmentally benign approaches were proposed and investigated, which include, but not

* Corresponding author. The Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China. Tel./fax: +86 755 26536141.

E-mail address: xiely@mail.ustc.edu.cn (L. Xie).

limited to, the usage of elastomers with low surface energy [8–14], the creation of different surface topographies [15–19] and the furry surfaces [20,21], the utilization of various surface chemistry [22–29] and enzymes [30,31], the application of a pulse electrical field [32], and the inclusion of antifoulants made of natural products [33–36].

More recently, soft and wet materials, such as hydrogels, have attracted more attention as some potentially useful and environmentally benign antifouling approaches [37–46]. Jiang et al. [41,42] demonstrated the hydrophilic materials, especially hydrolyzable zwitterionic materials and their derivatives have good non-fouling properties. Ekblad et al. [37] showed that poly(ethylene glycol)-containing hydrogel is very effective in slowing down the settlement and promoting the antifouling. Katsuyama et al. [38] found that acidic hydrogels of PAMPS and PAA, especially PAA, inhibit germination to the zoospores originating from *Laminaria angustata*. Murotsuki et al. [39] demonstrated that a set of synthetic hydrogels and PDMS elastomer can lead to less or no cyprids settlement than a polystyrene control. These are just some proofs of the concept. In reality, after the absorption of water, soft hydrogels are easily damaged by an external force and not strongly adhesive to a surface. Therefore, it is difficult, if not impossible, to apply them on a ship surface, which restrains their field tests and real applications.

In this study, we propose to synthesize a set of resins, i.e., copolymers made of different ratios of methyl methacrylate (MMA), acrylic acid (AA) and tributylsilyl methacrylate (TBSM). Each resin is then mixed with polyfunctional axiridine crosslinker (XAMA 7) in an equal stoichiometric ratio before coating it on a surface. The cross-linking reaction inside the coating gradually results in a hard and hydrophobic film. Note that the tributylsilyl ester group in the copolymer is hydrolyzable. Its hydrolysis in seawater can gradually lead to the formation of a layer of hydrogel on the top of the coating. As the hydrolysis continues, some polymer chains are broken and washed away so that the under layer is further exposed to seawater. Such a process progresses from surface to inside until the coating is completely removed. Therefore, this hydrogel-generating and self-peeling approach makes the surface layer of the coating antifouling, while the hydrophobic resin inside provides adhesion force and mechanical property, as schematically shown in Fig. 1. More important, such a coating can be easily applied to a ship surface by brushing or spraying. In this paper, we mainly prove our concept and correlate the antifouling ability of such prepared resins with their water adsorption contents and surface energies.

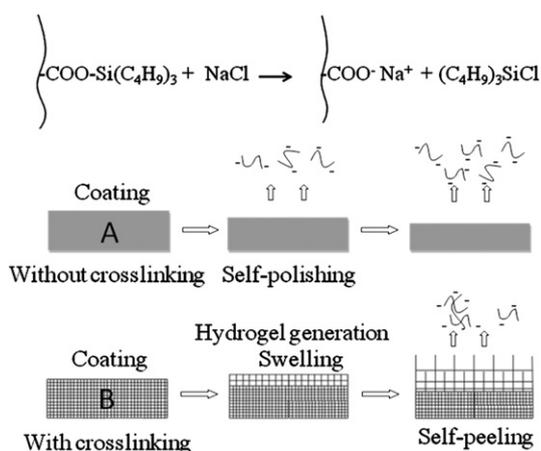


Fig. 1. Schematic of self-polishing and hydrogel-generating-and-self-peeling of novel coatings immersed in seawater.

2. Materials and methods

2.1. Reagents

Xylene, n-butyl acetate, methyl methacrylate (MMA), acrylic acid (AA), azobisisobutyronitrile (AIBN) were purchased from Alfa Co. Tributylsilyl methacrylate (TBSM) and polyfunctional axiridine cross-linking agent (XAMA 7) were kindly provided by Yuki Gosei Kogyo Co., and Bayer Co., respectively. AIBN was recrystallization three times from acetone. Artificial seawater (ASW) was prepared according to D1141-98 [47]. Other reagents were used as received without further purification.

2.2. Synthesis of copolymer resin

Considering their real applications, copolymer resins were prepared in solution that can be directly mixed with the cross-linking agent and applied on a surface. The copolymers were synthesized by free radical polymerization as follows. The solvent, xylene or a mixture of xylene and n-butyl acetate, was first placed in a 5-necked flask equipped with an agitator, a reflux condenser, a thermometer and a dropping funnel. The solvent was heated to 90 °C under nitrogen and then a mixture of nitrogen-purged monomers and initiator was added dropwise into the flask at a constant speed over a period of 4 h. The polymerization continued for another 4 h at 90 °C. The molar masses of resultant copolymers are in the range 1.4–3.0 × 10⁴ g/mol Table 1 summarizes chemical compositions of different reactive mixtures used in this study.

2.3. Coating preparation and biofouling test

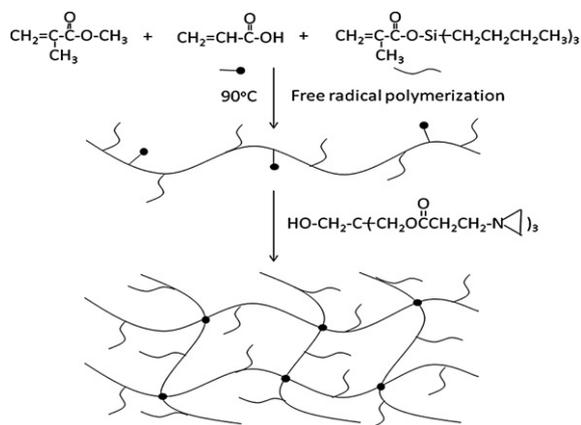
Coatings 1 and 2 were made from the solutions of Copolymers 1 and 2, respectively, without adding any cross-linking agent. Coatings 3–6 were prepared by mixing the solutions of Copolymers 3–6, respectively, with XAMA 7 in an equal stoichiometric ratio at the room temperature for about 30 min. Scheme 1 shows the resin synthesis and the coating formation. In the weight-loss, contact angle, ATR-FTIR, SEM, and water-adsorption measurements, each coating was applied on a glass slide with a film applicator and the film thickness was ~300 μm. Coatings 3–6 were dried at 25 °C for 2 days and then at 80 °C for one more day. Coating 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.

The antifouling test in shallow submergence follows GB 5370-2007 procedure. Each PMMA panel (300 × 200 × 3 mm³) was rubbed with a sandpaper. The coating was applied on each panel with a paintbrush to form a thin film of ~600 μm in thickness. Finally, the coatings were dried at 25 °C for 2 days and then at 80 °C for one more day. For each coating, three identical panels were prepared and attached to a frame so that they were submerged in a 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⁻¹) at Xiamen, China (24°45'N,

Table 1

Compositions of copolymerization for preparation of different resins, where amount of initiator (AIBN) was kept at 0.8 g and reaction temperature was 90.0 °C.

Copolymer	1	2	3	4	5	6
Xylene/g	100.0	100.0	90.0	90.0	90.0	90.0
n-butyl acetate/g			10.0	10.0	10.0	10.0
MMA/g	51.8	59.8	50.0	54.0	58.0	62.0
TBSM/g	48.2	40.2	48.2	44.2	40.2	36.2
AA/g			1.8	1.8	1.8	1.8



Scheme 1. Schematic illustration of resin synthesis and coating preparation.

118°07'E), on August 13, 2009. During each observation, the testing panels were taken out of the sea, gently washed with seawater and photographed. We used the number of barnacles settled on each panel to quantify the biofouling extent because barnacles are main macro-foulers on our panels.

2.4. Contact angle, ATR-FTIR and SEM measurements

Samples were immersed in ASW for different time periods, then taken out and immersed in distilled water for 5 min. The contact angle and ATR-FTIR measurements were conducted after the coatings were dried at room temperature for 2 days, using a Powereach JC2000C Optical Contact Angle Meter with Milli-Q water

and Nicolet 8700 FTIR Spectrometer, respectively. For SEM, coatings were measured after freeze-dried for 12 h using Hitachi S-3400 Scanning Electron Microscope. The contact-angle measurement is as follows. One little drop of water is formed on the tip of a micropipettor by controlling a manual liquid dispenser. After the glass slide on a raising platform contacts the drop, it is lowered to detach the drop from the micropipettor. After the contact angle keeps steady state, the image is recorded to determine the contact angle. Five different points were measured for each sample.

2.5. Weight-loss and water-adsorption measurement

Each dry coated glass slide was weighted (W_0) before dipping into a tank of artificial seawater (ASW) that was changed every two days. After different time periods, the glass slides were taken out of ASW, immersed in distilled water for 5 min and then gently dried with tissue before their weights ($W_{t,\text{wet}}$) were recorded. In parallel, some of these glass slides were dried at 25 °C for one day and then at 100 °C for 6 h before their weights ($W_{t,\text{dry}}$) were recorded. The weight difference between $W_{t,\text{wet}}$ and W_0 reflects the water adsorption of each coating. On the other hand, the weight difference between W_0 and $W_{t,\text{dry}}$ shows the weight-loss of each coating, which can be converted to the thickness change ($\Delta_{\text{thickness}}$) for a given density and coating size. For each resin, three coated glass slides were prepared and tested.

3. Results and discussion

Fig. 1 schematically shows the difference between the self-polishing (SP) and hydrogel-generating-and-self-peeling (HGSP)

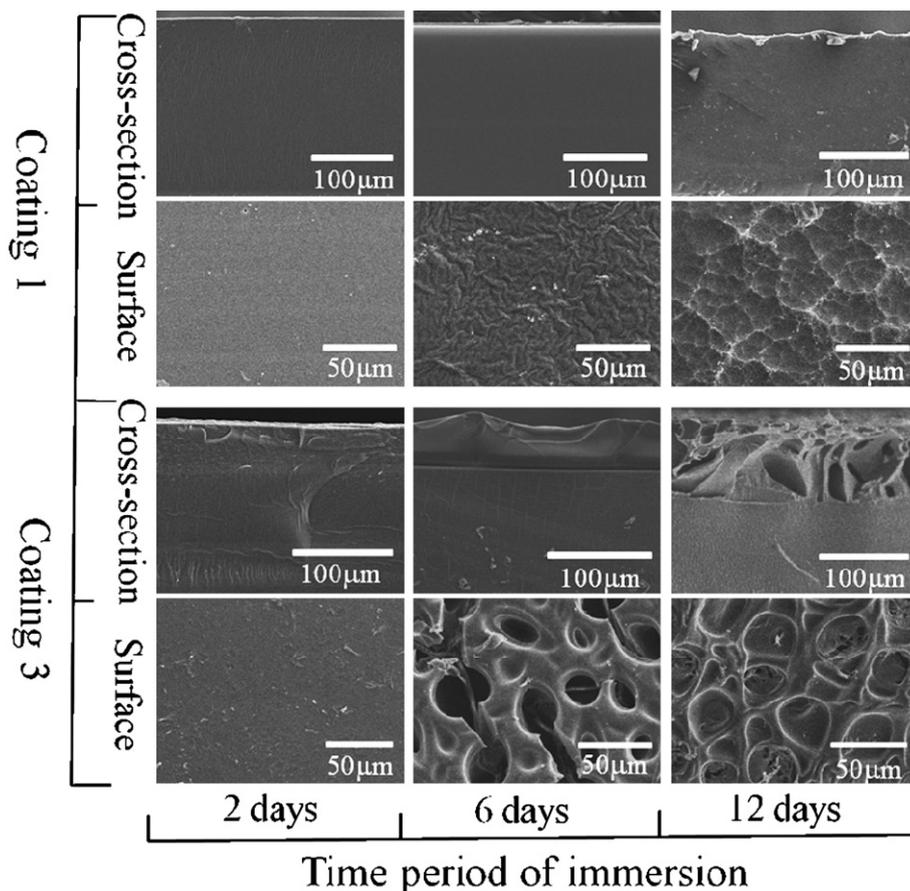


Fig. 2. SEM images of cross-section and surface of coatings 1 and 3 after different immersion-times.

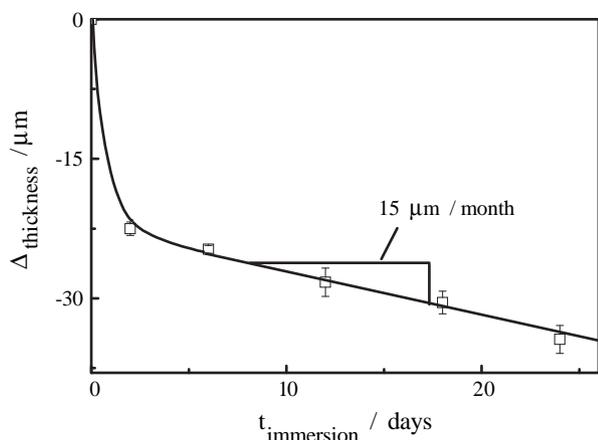


Fig. 3. Immersion-time dependence of thickness change of coating 1 in seawater.

coatings after they are immersed in seawater. Without any cross-linking (Coatings 1 and 2), the copolymer chains in the coating gradually swell in seawater so that they are slowly hydrolyzed from the top to bottom layer and become soluble. With the cross-linking (Coatings 3–6), the top layer swells to form a thin layer of soft and dynamic hydrogel. Only after a sufficient number of cross-linking bonds are hydrolyzed and broken, fragments of the gel network can start to be washed away, i.e., the self-peeling starts at this point. The difference can be visualized by SEM images (Fig. 2). For Coating 3, the self-generating and thickening of the top hydrogel layer is visible in the cross-section SEM images but such a hydrogel layer does not exist in Coating 1. In addition, the washing-away of fragments of the gel network leaves lots of holes on the surface of Coating 3. As the washing-away proceeds, the self-peeling is gradually achieved.

Fig. 3 shows that for Coating 1, besides an initial drop, the decrease of the coating thickness due to the self-polishing reaches a stable rate after 2 days. For Coatings 3–6, a thin layer of soft hydrogel was formed when they were immersed in seawater because of the cross-linking. After removing the top hydrogel layer, we found that the under layer of the coating was still very hard and hydrophobic.

Fig. 4 shows the immersion-time dependent relative weight-loss of Coatings 1, 3 and 5 in ASW. There is an initial fast weight-loss for all the coatings tested, presumably caused by a quick release of some low molar mass components, such residual

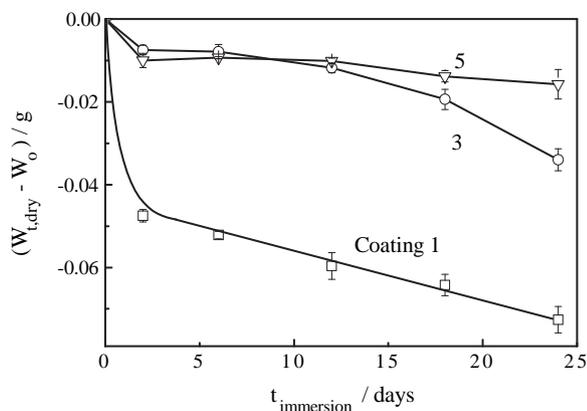


Fig. 4. Immersion-time dependence of relative weight-loss of different coatings in seawater; the coatings were prepared on glass slides ($25.4 \times 76.2 \text{ mm}^2$)

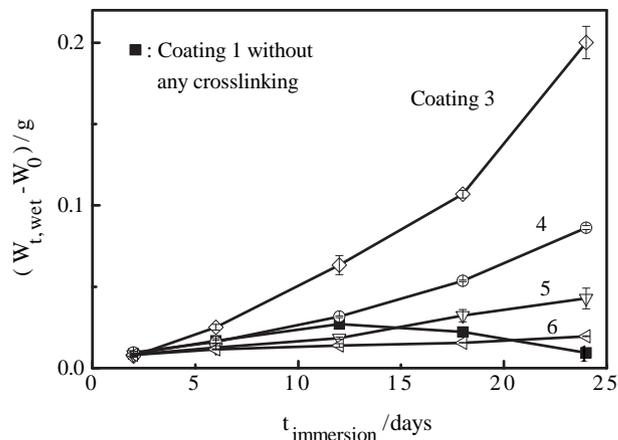


Fig. 5. Immersion-time dependence of relative weight-gain of different coatings in seawater; the coatings were prepared on glass slides ($25.4 \times 76.2 \text{ mm}^2$).

solvents and un-reacted monomers [48]. After two days, the weight-loss rate of Coating 1 becomes stable. As expected, the initial weight-loss of both Coatings 3 and 5 was smaller because of the cross-linking and the higher heating temperature ($80 \text{ }^\circ\text{C}$) in the coating preparation. After two days, the overall weight-loss rate of Coatings 3 and 5 is slower than that of Coating 1 as the initial hydrolysis only swells the top layer of the coating to form a hydrogel, not leading to much of its dissolution in seawater, because of the cross-linking. Fig. 4 also shows that after a long-time immersion in seawater, Coating 3 with a higher hydrolyzable TBSM content loses more weight than Coating 5 as the hydrogel network is gradually broken into soluble copolymer chains or fragments.

Fig. 5 shows that the wet-weight of Coating 1 ($W_{t,wet}$) increases in the first 12 days after it is immersed in seawater and then starts to decrease at a stable rate. Note that there is a competition between the absorption of water and the leaching-out of hydrolyzed copolymer chains for coatings without any cross-linking. Initially, the adsorption is dominant so that $W_{t,wet}$ increases. Finally, the adsorption is saturated and the leaching-out takes over, which explains why $W_{t,wet}$ starts to decrease after a while. For Coatings 3–6 with the cross-linking, $W_{t,wet}$ gradually increases with the immersion-time, presumably because further hydrolysis of tributylsilyl ester bond increases the thickness and water absorption of the hydrogel layer. As expected, $W_{t,wet}$ increases with the TBSM content for a given immersion-time period.

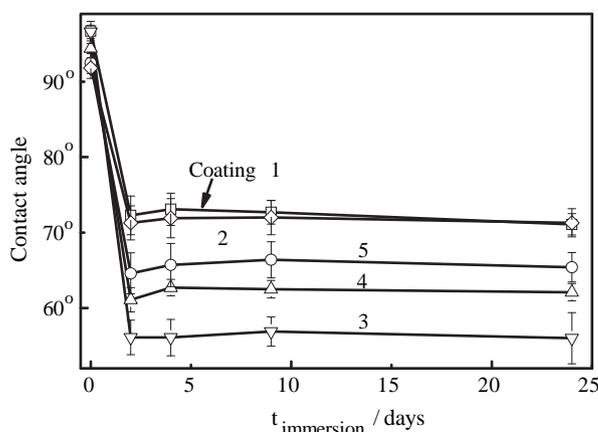


Fig. 6. Immersion-time dependence of contact angle of different coatings in seawater.

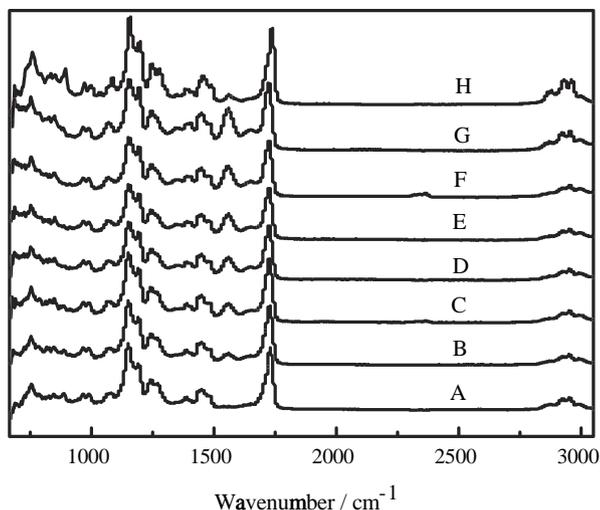


Fig. 7. ATR-FTIR spectra of surfaces of Coatings; A, B, C, D, E, F, G were coating 3 after immersed in artificial seawater for 0, 2, 4, 8, 24, 72, 120 h, respectively. H was coating 1 after immersed in artificial seawater for 120 h.

Fig. 6 shows that the coatings are hydrophobic with a contact angle higher than 90° before immersed into seawater. The higher the tributylsilyl ester content, the higher the contact angle is. After immersed in seawater for four days, the contact angle of each coating reaches a stable value. As expected, more tributylsilyl 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 a lower contact angle and higher water content. Those sufficiently hydrolyzed chains in Coatings 1 and 2 with no cross-linking become soluble in seawater and leach out, which explains why there is no difference between them in terms of the contact angle. The lower contact angle of Coatings 3–5 reveals that the thin hydrogel layer formed on the top of each coating is more hydrophilic than the hair-like layer (made of dangling chains) on Coatings 1 and 2. In comparison with coatings without any cross-linking, polymer chains inside the hydrogel network can be more hydrolyzed without being leaching-out due to the cross-linking. It has been known that the more hydrophilic the chain, the lower the contact angle is.

The result of the contact angle measurement can be supported by ATR-FTIR spectra. Asymmetrical stretching vibration of carboxylic anion shows the peak at approximately 1560 cm^{-1} . From **Fig. 7**, we can see the generation and increase of carboxylic anions at the surface of Coating 3 after immersion in the artificial seawater. The initial increase is fast in the first day of immersion, and then becomes slow. Comparing spectrum G with H, we can find that there are more carboxylic anions in the surface of the cross-linking coatings.

Figs. 8 and 9 show that for a given coating, barnacles grow more when the panel is immersed deeper between 1.30 and 1.65 m. The number of barnacles grown on the panel dramatically decreases when the copolymer chains in the resin are cross-linked. For Coatings 3–6 with the cross-linking, the antifouling ability clearly increases with the TBSM content. Meanwhile for Coating 3–6, the more TBSM content, the “cleaner” the surface is. In order to explain such a trend in **Fig. 9**, we will try to discuss and relate the antifouling ability of a coating to its surface property and water absorption as follows.

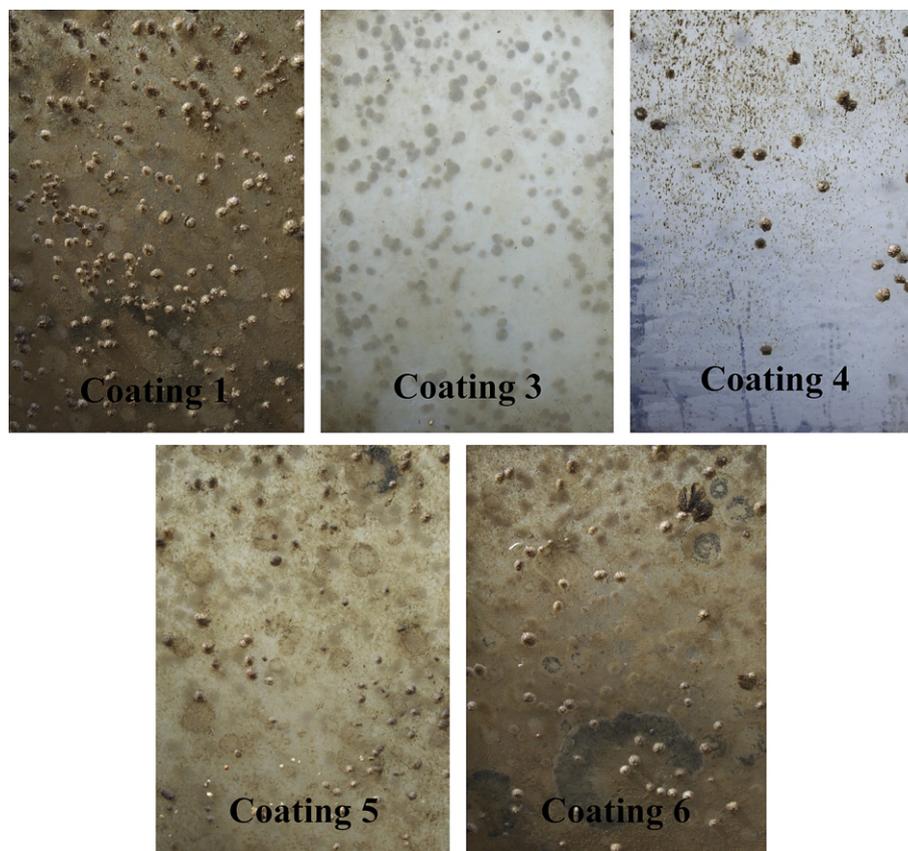


Fig. 8. Typical photographs of field-tested coatings submerged in a depth interval 1.30–1.65 m after two months.

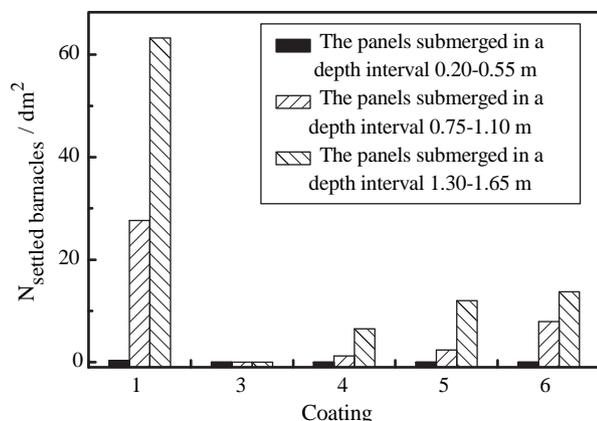


Fig. 9. Average density of barnacle *Balanus albicostatus* on field-tested six coatings immersed in seawater at different depths after two months.

It has been proposed that hydrophilic non-fouling surfaces prevent the protein adsorption and biofouling by creating a strong surface hydration layer [44,46,49–52]. It was claimed that there is a connection between biofouling and retention/release bound water molecules from a surface. Murosaki et al. [39] showed that the hydrophilic surfaces were not a favourable location for the settlement of cyprid larvae of barnacles. In comparison, there were less or even no cyprids settle, “methamorphose” on a set of hydrogels than a polystyrene plate (control) in their laboratory tests. The real marine environment is more complicated because organics can gradually accumulate on the surface, and living matters, such as bacteria, single-cell diatoms, protozoa and rotifer, gradually colonize on a surface to form a thin film of biological species which would change the character of surface. For our samples, the coating with a higher TBSM content hydrolyzes more. Without any cross-linking, individual chains with sufficient hydrolyzation leach out. In contrast, the cross-linking prevents the leaching-out of highly hydrolyzed chains so that the surface is more negatively charged with more tightly bound water molecules, making the adsorption of proteins on it more difficult. Moreover, the self-peeling property can continuously self-generate a new layer of hydrogel and maintain non-fouling character of the surface. This correlates well with its higher anti-biofouling ability.

4. Conclusion

A new kind of antifouling coatings made of cross-linked poly(methyl methacrylate-co-tributylsilyl methacrylate-co-acrylic acid) terpolymer chains have been successfully developed by a combination of the hydrogel-generating and self-peeling properties. After immersed into seawater, the tributylsilyl ester bonds in the top layer of each coating gradually hydrolyze into anionic and hydrophilic carboxylic groups to form a thin layer of hydrogel. Meanwhile, the under-layer cross-linked chains still remain hydrophobic and can provide a sufficient adhesive force and mechanical strength. Our field tests showed that most of the coatings are intact after it is submerged in seawater for 2 months. Our results have clearly demonstrated that the gradual formation and peeling-off of a thin layer of highly swollen hydrogel on the coating surface can affectively slow down the biofouling. In general, increasing the hydrolyzable TBSM content inside a coating increases its antifouling ability, which is well correlated to its more hydrophilic surface with more water molecules bound on the surface, directly reflected in its lower contact angle and higher water adsorption. In contrast, the coatings made of identical

polymer resin without any cross-linking, i.e., only with the self-polishing property, is relatively less effective in anti-biofouling, presumably because the chains are leaching-out when the hydrolysis reaches a certain degree. Therefore, the self-hydrogel-generating-and-self-peeling idea has been conceptually proven by the current study. These newly developed anti-biofouling paints are readily coated on a surface, such as metal, plastic or wood, by a conventional method, brushing or spraying or dipping.

Acknowledgements

The financial support of Ministry of Science and Technology of China (2007CB936401), the National Natural Scientific Foundation of China (NNSFC) Projects (20934005, 50773077 and 21004040), the National High Technology Research and Development Program of China (2009AA03Z513), and the Hong Kong Special Administration Region Earmarked Project (CUHK4039/08P, 2160361) is gratefully acknowledged.

References

- [1] Chambers LD, Stokes KR, Walsh FC, Wood RJK. *Surf Coat Tech* 2006;201(6):3642–52.
- [2] Dobretsov S, Dahms HU, Qian PY. *Biofouling* 2006;22(1):43–54.
- [3] Yebra DM, Kiil S, Dam-Johansen K. *Prog Org Coat* 2004;50(2):75–104.
- [4] Champ MA. *Sci Total Environ* 2000;258(1–2):21–71.
- [5] Abbott A, Abel PD, Arnold DW, Milne A. *Sci Total Environ* 2000;258(1–2):5–19.
- [6] Mukherjee A, Rao KVM, Ramesh US. *J Environ Manage* 2009;90:S51–9.
- [7] Singh N, Turner A. *Mar Pollut Bull* 2009;58(4):559–64.
- [8] Baier RE. *J Mater Sci Mater M* 2006;17(11):1057–62.
- [9] Genzer J, Efimenko K. *Biofouling* 2006;22(5):339–60.
- [10] Sun YJ, Guo SL, Walker GC, Kavanagh CJ, Swain GW. *Biofouling* 2004;20(6):279–89.
- [11] Chaudhury MK, Finlay JA, Chung JY, Callow ME, Callow JA. *Biofouling* 2005;21(1):41–8.
- [12] Wendt DE, Kowalke GL, Kim J, Singer IL. *Biofouling* 2006;22(1):1–9.
- [13] Brady RF. *Prog Org Coat* 2001;43(1–3):188–92.
- [14] Hu ZK, Finlay JA, Chen L, Betts DE, Hillmyer MA, Callow ME, et al. *Macromolecules* 2009;42(18):6999–7007.
- [15] Lemire M, Bourget E. *Mar Ecol Prog Ser* 1996;135(1–3):77–87.
- [16] Hills JM, Thomason JC, Muhl J. *Funct Cell* 1999;13(6):868–75.
- [17] Schumacher JF, Carman ML, Estes TG, Feinberg AW, Wilson LH, Callow ME, et al. *Biofouling* 2007;23(1):55–62.
- [18] Schumacher JF, Aldred N, Callow ME, Finlay JA, Callow JA, Clare AS, et al. *Biofouling* 2007;23(5):307–17.
- [19] Callow ME, Jennings AR, Brennan AB, Seegert CE, Gibson A, Wilson L, et al. *Biofouling* 2002;18(3):237–45.
- [20] Scardino AJ, Harvey E, De Nys R. *Biofouling* 2006;22(1):55–60.
- [21] Baum C, Meyer W, Stelzer R, Fleischer LG, Siebers D. *Mar Biol* 2002;140(3):653–7.
- [22] Gudipati CS, Finlay JA, Callow JA, Callow ME, Wooley KL. *Langmuir* 2005;21(7):3044–53.
- [23] Huggett MJ, Nedved BT, Hadfield MG. *Biofouling* 2009;25(5):387–99.
- [24] Bi XY, Xu H, Lai SL, Yang KL. *Biofouling* 2009;25(5):435–44.
- [25] Krishnan S, Wang N, Ober CK, Finlay JA, Callow ME, Callow JA, et al. *Biomacromolecules* 2006;7(5):1449–62.
- [26] Hu ZK, Chen L, Betts DE, Pandya A, Hillmyer MA, DeSimone JM. *J Am Chem Soc* 2008;130(43):14244–52.
- [27] Hu ZK, Pandya AA, DeSimone JM. *Abstr Pap Am Chem Soc* 2008;236 [–].
- [28] Berndt E, Behnke S, Dannehl A, Gajda A, Wingender J, Ulbricht M. *Polymer* 2010;51(25):5910–20.
- [29] Goddard JM, Hotchkiss JH. *Prog Polym Sci* 2007;32(7):698–725.
- [30] Olsen SM, Pedersen LT, Laursen MH, Kiil S, Dam-Johansen K. *Biofouling* 2007;23(5):369–83.
- [31] Aldred N, Phang IY, Conlan SL, Clare AS, Vancso GJ. *Biofouling* 2008;24(2):97–107.
- [32] Perez-Roa RE, Anderson MA, Rittschof D, Orihuela B, Wendt D, Kowalke GL, et al. *Biofouling* 2008;24(3):177–84.
- [33] Zhou XJ, Zhang Z, Xu Y, Jin CL, He HP, Hao XJ, et al. *Biofouling* 2009;25(1):69–76.
- [34] Feng DQ, Ke CH, Lu CY, Li SJ. *Biofouling* 2009;25(3):181–90.
- [35] Angarano MB, McMahon RF, Hawkins DL, Schetz JA. *Biofouling* 2007;23(5):295–305.
- [36] Clare AS. *Biofouling* 1996;9:211–99.
- [37] Ekblad T, Bergstroem G, Ederth T, Conlan SL, Mutton R, Clare AS, et al. *Biomacromolecules* 2008;9(10):2775–83.

- [38] Katsuyama Y, Kurokawa T, Kaneko T, Gong JP, Osada Y, Yotsukura N, et al. *Macromol Biosci* 2002;2(4):163–9.
- [39] Murosaki T, Noguchi T, Kakugo A, Putra A, Kurokawa T, Furukawa H, et al. *Biofouling* 2009;25(4):313–20.
- [40] Chen SF, Jiang SY. *Adv Mater* 2008;20(2):335.
- [41] Chen SF, Liu LY, Jiang SY. *Langmuir* 2006;22(6):2418–21.
- [42] Chen SF, Zheng J, Li LY, Jiang SY. *J Am Chem Soc* 2005;127(41):14473–8.
- [43] Zhang Z, Finlay JA, Wang LF, Gao Y, Callow JA, Callow ME, et al. *Langmuir* 2009;25(23):13516–21.
- [44] Hower JC, Bernards MT, Chen SF, Tsao HK, Sheng YJ, Jiang SY. *J Phys Chem B* 2009;113(1):197–201.
- [45] Jiang SY, Cao ZQ. *Adv Mater* 2010;22(9):920–32.
- [46] Zheng J, Li LY, Chen SF, Jiang SY. *Langmuir* 2004;20(20):8931–8.
- [47] ASTM. Standard practice for the preparation of substitute Ocean water. vol. D 1141 – 98; 2003. p. 3.
- [48] Yonehara Y, Yamashita H, Kawamura C, Itoh K. *Prog Org Coat* 2001;42(3–4):150–8.
- [49] Ostuni E, Chapman RG, Holmlin RE, Takayama S, Whitesides GM. *Langmuir* 2001;17(18):5605–20.
- [50] Jeon JHL, SI, Andrade JD, De Gennes PG. *J Colloid Interface Sci* 1991;142:149–58.
- [51] Besseling NAM. *Langmuir* 1997;13(7):2113–22.
- [52] Vanderah DJ, La HL, Naff J, Silin V, Rubinson KA. *J Am Chem Soc* 2004;126(42):13639–41.