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Self-repairing silicone coatings for marine anti-biofouling†

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Marine biofouling is one of the most challenging problems today. Silicone polymer based coatings with a low surface energy and elastic modulus can effectively inhibit or release biofouling. However, their non-repairable properties and poor antifouling ability under static conditions limit their applications. Here, we report a self-repairing coating consisting of poly(dimethylsiloxane) based polyurea (PDMS-PUa) and a small amount of organic antifoulant (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one) (DCOIT). The coating can completely recover its mechanical properties after damage either in air or artificial seawater at room temperature. Such recovery can be accelerated at a higher temperature. Moreover, the release rate of DCOIT is almost constant and can be regulated by its concentration. Six-month marine field tests demonstrate that the system has a good antifouling/fouling release performance even under static conditions.

Introduction

Marine biofouling formed by settlement and accumulation of microorganisms, plants and animals on surfaces immersed in seawater profoundly influences maritime industries. It accelerates biocorrosion, increases hydrodynamic drag and therefore increases fuel consumption and transports invasive species.[1] A coating containing tributyltin (TBT) was the most effective system to combat marine biofouling, but it has been globally banned since 2008 due to its persistent toxicity to marine organisms.[2–4] Today, we are faced with the task of developing environment-friendly and effective antifouling systems. Besides organic antifoulants,[5–7] polymeric materials such as self-polishing copolymers,[8,9] biodegradable polymers,[10–12] protein resistant polymers,[13–16] and amphiphilic polymers[17–20] have been prepared for this purpose. Particularly, poly(dimethylsiloxane) (PDMS) elastomers provide minimal adhesion strength for fouling organisms due to their low surface energy and elastic modulus so that marine organisms only weakly adhere to the surface and can be readily removed by shear forces.[21–23] Moreover, the coating has a smooth surface, which can reduce the drag force and fuel consumption of ships. However, they are only effective for high-speed vessels (15 > knots), and they exhibit poor antifouling performance under static conditions.[24] PDMS elastomers also have poor mechanical properties and adhesion to substrates, so they suffer from peeling or damaging in service. Even worse, they are hard to repair once damaged due to their cross-linked network structure.

To improve mechanical properties, PDMS elastomers are physically modified *via* incorporation of nanoparticles or carbon nanotubes[25,26] or chemically modified with epoxy[27,28] and polyurethane.[29,30] Unfortunately, these approaches usually lead to the increase of the surface energy and elastic modulus and thus reduce the antifouling ability. Grafting zwitterionic[31] or antimicrobial polymers[32,33] to PDMS could improve its static antifouling performance. Yet, the modified PDMS swollen in marine environments would detach from the substrate.

Self-repairing or self-healing polymers have the built-in ability to repair themselves after damage. The self-repairing is usually driven by hydrogen bond interaction, the Diels–Alder reaction or incorporating microcapsules into polymers.[34–38] Such a system can be recovered to its original state in mechanical strength, shape and surface properties, which provides a new strategy to develop high performance PDMS elastomer based antifouling materials.

In the present study, we have developed a PDMS based polyurea (PDMS-PUa) whose urea groups and PDMS segments allow it to exhibit excellent self-repairing and good adhesion to substrates. PDMS-PUa also acts as the carrier of the organic antifoulant (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one, DCOIT) and realizes its controlled release even under static conditions, where DCOIT is a relatively environment-friendly antifoulant since DCOIT has been granted by the European Union (EU) and US Environmental Protection Agency (EPA) due to its rapid degradation in marine environments with a half-life of <24 h in seawater and <1 h in sediment.[39] We report the self-repairing and antifouling performance of the anti-biofouling system in the laboratory and marine field. Our aim is to develop high performance antifouling coatings.

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Experimental section

Materials

α,ω-Aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS) ($M_w = 2000$ g mol^{-1}) from Hangzhou Silong Mater. Tech. Co., Ltd. was dried under reduced pressure for 2 h prior to use. Commercially available acrylic resin (AR) was purchased from Mitsubishi. Isophorone diisocyanate (IPDI, 99%) from Aladdin was used as received. Tetrahydrofuran (THF, ≥99%) and isopropyl alcohol (IPA, ≥99.5%) from Sinopharm were refluxed over CaH_2 and distilled prior to use. 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOIT) was kindly presented by Thankful New Material Co., Ltd. PDMS elastomer (Sylgard 184) was purchased from Dow Corning. Artificial seawater (ASW) was prepared according to ASTM D1141. Other reagents were used as received.

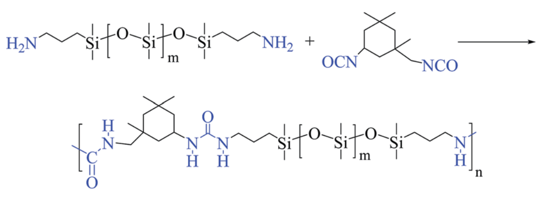
Preparation of PDMS-PUa

PDMS-PUa was synthesized from α,ω-aminopropyl terminated poly(dimethylsiloxane) and isophorone diisocyanate (IPDI) (Scheme 1) and the structure was confirmed by FTIR and ^{1}H NMR (Fig. S1 and S2†). Typically, 2.23 g (0.01 mol) of IPDI was dissolved in 12 mL of THF and then poured into a three necked round bottom flask with a condenser, dropping funnel, nitrogen gas inlet and magnetic stirrer bar. 20.0 g (0.01 mol) of APT-PDMS was dissolved in 100 mL of THF and the solution was added dropwise under a nitrogen atmosphere in 1 h. The mixture was stirred for another 3 h under nitrogen at room temperature. The reaction was monitored by FTIR. When the band at 2260 cm^{-1} for isocyanate completely disappeared, the reaction mixture was precipitated in excess water and dried under vacuum for 24 h.

PDMS-PUa with different DCOIT contents was prepared by a solution mixing method. Typically, PDMS-PUa with 5.0 wt% DCOIT (PDMS-PUa/5.0) was prepared as follows: 5.00 g PDMS-PUa was dissolved in THF (30 mL) under stirring at 25 °C, and 0.2632 g DCOIT (5.0 wt%) was added into the PDMS-PUa solution and stirred until a homogeneous solution was obtained. Finally, the polymer mixture solution was casted on a substrate to form a polymeric film. Other PDMS-PUa solutions with 1.0 wt%, 2.5 wt% and 10.0 wt% DCOIT were prepared by the same procedure. For comparison, AR solutions with 1.0 wt%, 2.5 wt%, 5.0 wt% and 10.0 wt% DCOIT were also prepared.

Characterization

Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum was obtained on a Bruker VECTOR-22 FTIR spectrometer using the KBr disk method. The scanning range was 650–4000 cm^{-1} and the spectral resolution was 4 cm^{-1}.



Scheme 1 Synthesis of PDMS-PUa.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR). The ^{1}H NMR spectrum was recorded on a Bruker AV600 NMR (600 MHz) spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard.

Self-repairing of PDMS-PUa and PDMS-PUa/DCOIT mixtures. A polymer film was prepared by a solution casting method. The self-repairing of the polymer film in air or artificial seawater (ASW) at room temperature was recorded using a digital camera or an optical microscope.

Tensile test. A tensile test was performed using an Al-7000S Series (GOTECH Testing Machines Inc.) instrument equipped with a 100 N load cell at a speed of 25 mm min^{-1}. Three samples were tested for each polymer. A tensile experiment was performed at room temperature with a dog bone shaped sample (80 mm × 6 mm × 1 mm). For self-repairing tests, after the polymer film was cut into two pieces, they were gently joined together and kept attached for a certain time in air or ASW at room temperature. The sample was tested to obtain the stress–strain curve.

Adhesion test. A PosiTest AT-A Automatic adhesion tester from DeFelsko was used to measure the adhesion of PDMS-PUa or PDMS-PUa/DCOIT to a glass fiber reinforced epoxy resin substrate according to ASTM D4541. An aluminum dolly with a diameter of 20 mm was adhered to the surface of the polymer using epoxy adhesive. Pull-test adhesion data were obtained by detaching the dolly from the substrate at the speed of 0.2 MPa s^{-1}. Five different regions for each sample were tested to obtain an average value.

Determination of the DCOIT release rate. DCOIT concentration was measured by high performance liquid chromatography (HPLC) to determine its release rate under static conditions. Typically, a polymer film was prepared on an epoxy resin panel (20 mm × 70 mm), and then the panel was immersed in ASW. At a certain period of time, the panel was transferred from the holding tank to an individual measuring container with 100 mL fresh seawater. After 24 h of immersion, 10 mL of seawater was taken from the individual measuring container and extracted three times using 10 mL dichloromethane. After drying under nitrogen gas, the extract was resuspended in 100 μL methanol and then subjected to HPLC analysis using a reversed-phase system (Waters 2695) with a Phenomenex Luna C18 column connected to a photodiode array detector at 210 nm. The peaks for DCOIT were determined based on the retention time and its amount was calculated from the established standard curves using peak areas plotted against the known quantities of standards. The recovery efficiency for DCOIT analysis is 87.6%. The errors defined as relative standard deviations for the calculation of the release rate were less than 5.0%.

Marine field tests. Glass fiber reinforced epoxy resin panels (300 mm × 100 mm × 3 mm) were coated with samples at 25 °C and 53% of relative humidity. The thickness of the coating ranging from 250 to 300 μm was controlled by the weight of the polymer solution. The panels were exposed to seawater at a depth of 1 m at the inner Xiamen bay (24° 33′N, 118° 09′E) in

China, where fouling organisms are diversified and biofouling pressure is heavy. The panels were taken out of the sea periodically and carefully washed with seawater to observe and photograph the deposition of sea organisms and seaweed on the panels. An epoxy resin panel without any coating and panels coated with AR/DCOIT were used as the control and reference, respectively.

Result and discussion

PDMS-PUa was synthesized from α,ω-aminopropyl terminated poly(dimethylsiloxane) and isophorone diisocyanate (IPDI) (Scheme 1) and the structure was confirmed by FTIR and ^{1}H NMR (Fig. S1 and S2†). This polymer can reversibly cross-link at room temperature besides possessing elasticity and low surface energy properties due to the strong hydrogen bonding *via* urea groups and flexible PDMS soft segments in PDMS-PUa.[40] To improve the ultimate antifouling/fouling release performance (especially under static conditions), DCOIT (<10 wt%) is introduced into PDMS-PUa.

We examined the self-repairing properties of PDMS-PUa with or without addition of DCOIT (Fig. 1 and 2). The polymer film was cut into two pieces and then put together carefully without external pressure to allow repairing to happen at room temperature. After 48 h, the film was repaired spontaneously and the crack completely disappeared, indicating that PDMS-PUa can self-repair at room temperature. The time-dependent change of the crack in PDMS-PUa was first examined in air by using an optical microscope (Fig. 2 and S3†). The crack in the polymer film is gradually repaired with time and it completely disappears within 48 h. Interestingly, the addition of DCOIT does not reduce the self-repairing. All the coatings can completely self-repair within 48 h in the range we investigated (1.0–10.0 wt%). Actually, the PDMS-PUa and PDMS-PUa/DCOIT mixture can self-repair in ASW (Fig. S4†). This is important for the application of the materials in marine biofouling.

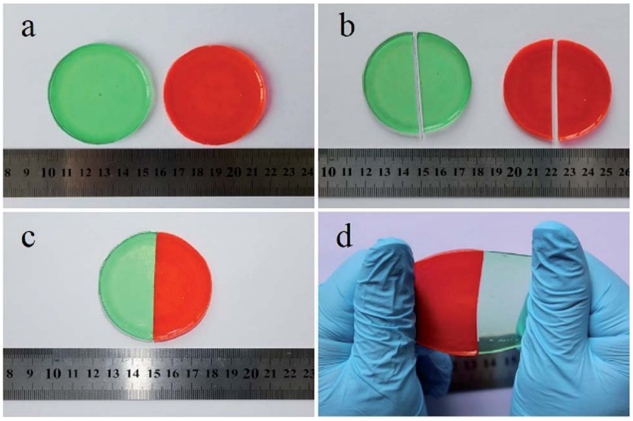


Fig. 1 Self-repairing of PDMS-PUa imaged by using a digital camera at 25 °C: (a) original sample; (b) damaged sample; (c) rejoined sample; (d) self-repairing sample for 48 h. For clear observation, the samples were dyed in red and green.

The stress–strain curves for self-repairing of PDMS-PUa as a function of time are shown in Fig. 3a. The original PDMS-PUa exhibits an ultimate strength of 0.81 MPa and an elongation of 551% (Table S1†). After 24 h of self-repairing, the stretchability of the damaged PDMS-PUa has already recovered, but the ultimate strength has not been restored. After 48 h, either the ultimate strength or the elongation of the damaged PDMS-PUa had been almost restored. The tensile strength of PDMS-PUa with different DCOIT contents was examined (Fig. 3b, S5 and Table S1†). As the DCOIT content increases, the ultimate strength decreases whereas the elongation at break and the self-repairing rate increase. Fig. 4 shows the DCOIT content dependence of the ultimate strength and repairing efficiency of PDMS-PU. Here, we use the ratio of toughness restored to the original value to evaluate the repairing efficiency. At a DCOIT content of 5.0 wt%, the ultimate strength is 0.44 MPa and the self-repairing efficiency is about 98%. When DCOIT reaches 10.0 wt%, the self-repairing efficiency is up to 100%, but the ultimate strength reduces to 0.22 MPa. Clearly, the self-repairing efficiency increases with the DCOIT content. This can be explained as follows. DCOIT molecules are embedded on PDMS-PUa chains due to the hydrogen bonding between the carbonyl group in DCOIT and NH in PDMS-PUa. On the other hand, the long alkyl chains (C8) in DCOIT space PDMS-PUa chains apart and reduce their interactions. Namely, DCOIT acts as a plastic agent for PDMS-PUa. Thus, PDMS-PUa chains become more mobile and the system becomes softer when they mix with DCOIT, leading to the decrease in ultimate strength but increase in self-repairing efficiency.

We also examined the stress–strain curves of the damaged PDMS-PUa or PDMS-PUa with 5.0 wt% DCOIT as a function of time in ASW (Fig. S6†). The ultimate strength gradually

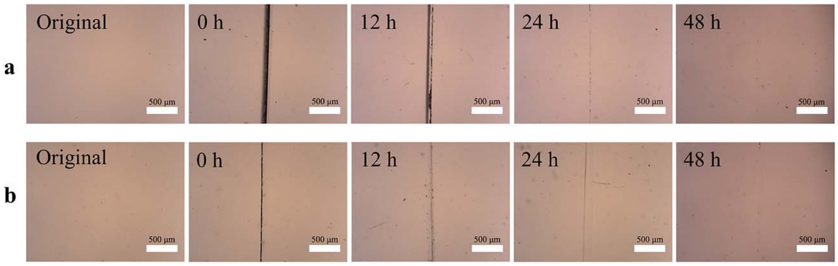


Fig. 2 Self-repairing process at room temperature imaged by using an optical microscope (500×): (a) PDMS-PUa and (b) PDMS-PUa with 5.0 wt% DCOIT.

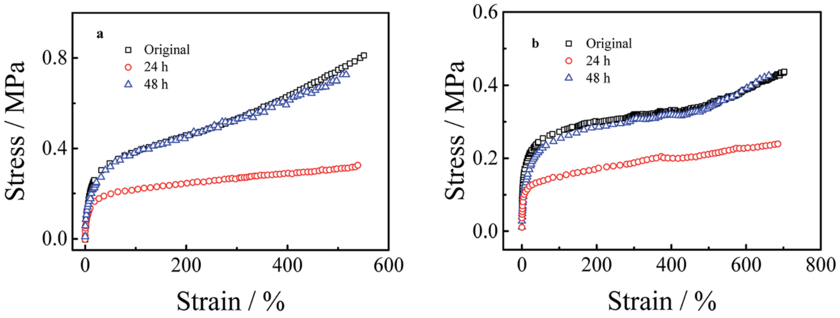


Fig. 3 Stress–strain curves of PDMS-PUa (a) and PDMS-PUa with 5.0 wt% DCOIT (b) at 25 °C.

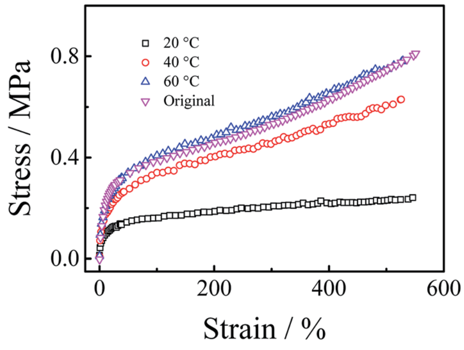


Fig. 5 Stress–strain curves of PDMS-PUa as a function of temperature, where the repairing time is 4 hours.

increases with time, indicating that the damaged polymer gradually recovered itself. After 48 h, the ultimate strength and elongation of the damaged polymers were almost restored, indicating that PDMS-PUa or PDMS-PUa/DCOIT holds self-repairing properties in marine environments. Actually, the repairing process can be accelerated by increasing the temperature (Fig. 5). The fact clearly indicates the self-repairing of PDMS-PUa arises from the breaking and reconstruction of hydrogen bonds, which are sensitive to temperature.

The adhesion strength to the substrate is critical for antifouling coatings. Fig. 6 shows the adhesion strength of PDMS-PUa and PDMS-PUa with different DCOIT contents. Clearly, the coating has adhesion strength above 1.0 MPa which slightly varies with the DCOIT content. Note that PDMS with low surface energy is bonded to the substrate *via* van der Waals interactions. Such weak interactions allow PDMS chains to migrate to the upper layer while the urea groups with strong interaction with the substrate tend to locate at the lower layer. In other words, PDMS-PUa has self-stratifying properties. Anyhow, the urea groups are responsible for the adhesion of PDMS-PUa/DCOIT to the substrate. That is why the adhesion strength slightly varies with the DCOIT content.

The release rate of the antifoulant plays a critical role in marine anti-biofouling. Quick release is favorable to anti-biofouling in a short time but shortens the service time. The release rate of DCOIT from the PDMS-PUa/DCOIT mixture within 6 months is shown in Fig. 7. The cumulative release can be found in Fig. S7.† For each PDMS-PUa/DCOIT sample, the release rate of DCOIT has a slight change in the initial stage but levels off in 30 days. As the DCOIT content increases from 1.0 wt% to 10 wt%, the release rate increases from 1.5 to 4.5 μg cm^{-2} d^{-1}. In other words, we can control the antifouling ability and service life of the system by regulating the amount of antifoulant. Note that the control sample (acrylic resin, AR) with 5.0 wt% DCOIT has a low release rate (<1.5 μg cm^{-2} d^{-1}) during the immersion period (180 days). As discussed above, DCOIT with a long alkyl chain (C8) is hydrophobic and has a low solubility (~5 ppm) in seawater.[41] Besides, the electron rich oxygen and nitrogen atoms in DCOIT have chemical affinity to the urea groups of PDMS-PUa. Therefore, it is prone to stay in the polymer matrix. However, it would migrate to the surface

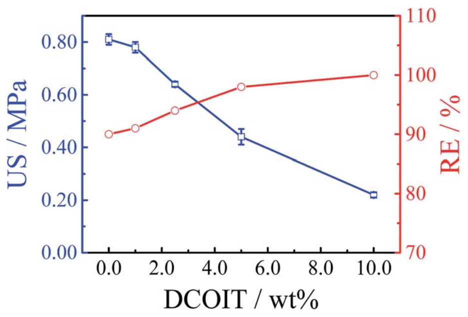


Fig. 4 DCOIT content dependence of the ultimate strength (US) and repairing efficiency (RE) of PDMS-PUa/DCOIT.

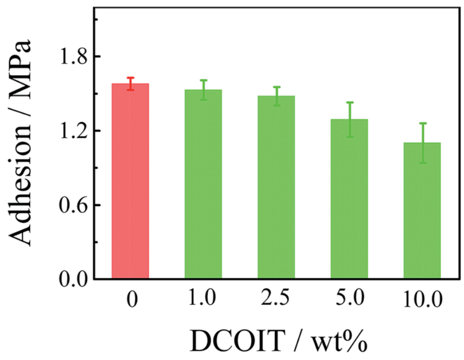


Fig. 6 DCOIT content dependence of the adhesion strength of PDMS-PUa/DCOIT.

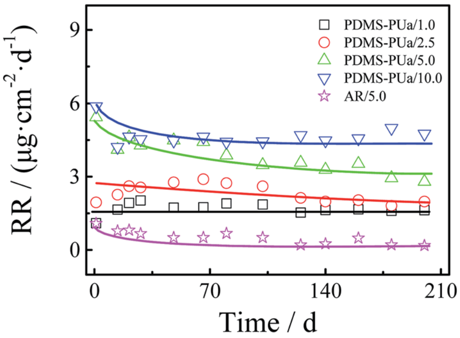


Fig. 7 Release rate (RR) of DCOIT in ASW at 25 °C.

driven by osmotic pressure and gradually dissolve into seawater. Therefore, DCOIT can be released slowly and constantly from PDMS-PUa. In other words, the self-repairing polymer leads to a linear controlled release for the antifoulant, making long-term antifouling possible.

The antifouling/fouling release performance of PDMS-PUa/DCOIT is examined by marine field tests. Fig. 8 shows the typical images of the tested panels after immersion in natural seawater for 90 and 180 days. Within 90 days, the control panel without any coatings is completely covered by fouling organisms including barnacles, mussels and sponges, indicating a heavy fouling pressure in the testing site. The panels with the PDMS or PDMS-PUa surface are covered by some hard fouling organisms after 90 days, but the coatings are completely fouled by organisms after 180 days, indicating that PDMS and PDMS-PUa have limited antifouling/fouling release performance under static conditions. For the panels coated with the PDMS-PUa/DCOIT mixture, almost no fouling organisms are observed on the surface in 90 days, even when the DCOIT content is as low as 1.0 wt%. After 180 days, PDMS-PUa with 1.0 wt% DCOIT is fouled by some microorganisms and a few barnacles whereas PDMS-PUa with 2.5 wt% DCOIT is only fouled by a few microalgae. Thus, PDMS-PUa/DCOIT has a good antifouling/fouling release performance when the DCOIT content is above 2.5 wt%. In contrast, all the panels coated with AR/DCOIT are completely covered by fouling organisms after 90 days, even when the DCOIT content is as high as 10.0 wt% (Fig. S8†). Note that the water contact angle and surface free energy of PDMS-PUa/DCOIT are close to those of PDMS-PUa (Fig. S9†). Namely, the addition of DCOIT does not change the surface hydrophobicity

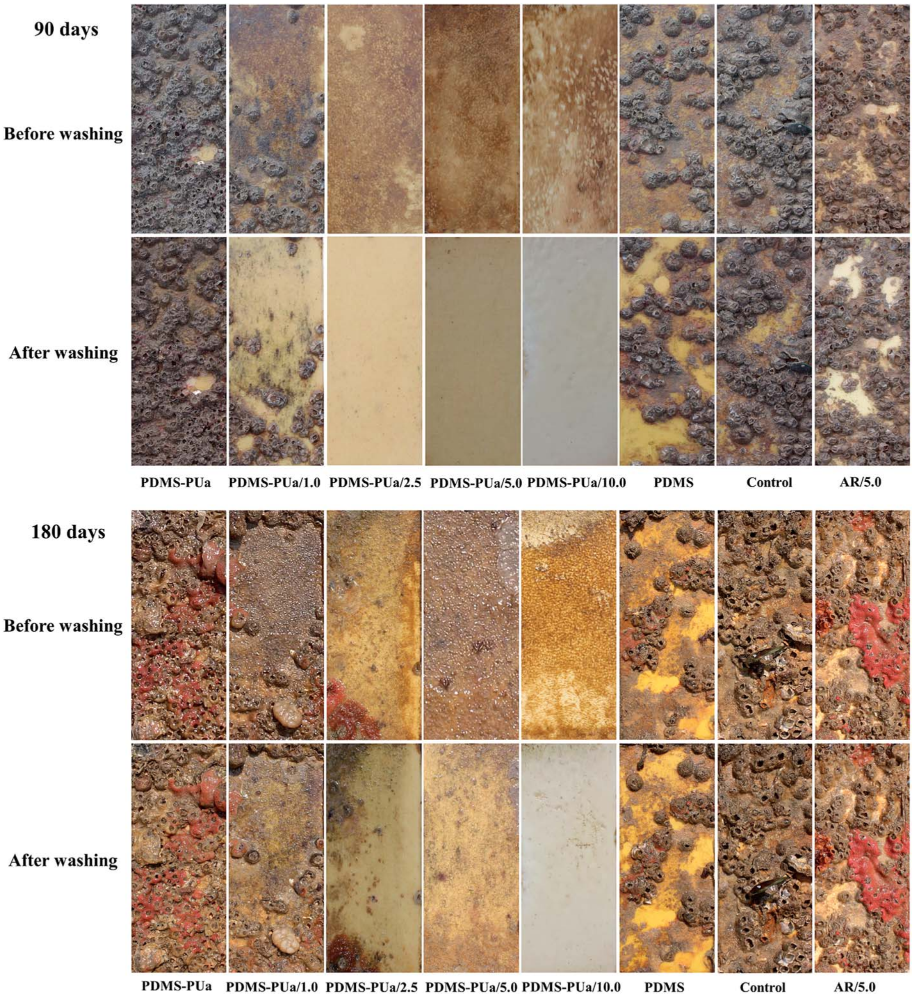


Fig. 8 Images of the tested panels coated with PDMS-PUa/DCOIT after immersion in seawater for 90 and 180 days.

and low surface free energy of PDMS-PUa, or PDMS-PUa/DCOIT still exhibits the same fouling release performance as PDMS-PUa. Thus, the combination of the fouling release performance of PDMS-PUa and the controlled release of DCOIT is responsible for the long-term antifouling performance of the system.

Conclusions

In conclusion, we have developed a self-repairing coating consisting of poly(dimethylsiloxane) based polyurea (PDMS-PUa) and a small amount of organic antifoulant (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one). Such a coating has good adhesion to substrates. The coating exhibits good self-repairing properties against damage at room temperature in either air or artificial seawater due to the breaking and reconstruction of hydrogen bonding. Such recovery can be accelerated by increasing the temperature. Moreover, the coating realizes the controlled release of the organic antifoulant. The release rate of DCOIT is almost constant and it can be regulated by its concentration. Marine field tests demonstrate that the coating has excellent antifouling/fouling release performance even under static conditions for more than six months. The coating is expected to find applications in marine anti-biofouling.

Acknowledgements

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