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Poly(dimethylsiloxane)-Based Polyurethane with Chemically Attached Antifoulants for Durable Marine Antibiofouling

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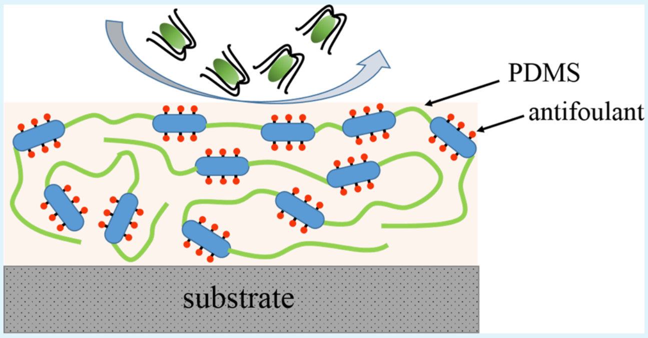
Supporting Information

ABSTRACT: Marine biofouling is a problem for marine industry and maritime activities. We have prepared polyurethane with poly(dimethylsiloxane) (PDMS) main chains and *N*-(2,4,6-trichlorophenyl) maleimide (TCM) pendant groups via a combination of a thiol−ene click reaction and a condensation reaction and studied its properties. The polymer has low surface energy and a high water contact angle. When TCM content in bulk is high enough, sufficient antifoulant groups can be exposed on the surface. Our study reveals that such polymeric surface can effectively inhibit the adhesion and colonization of marine organisms such as bacteria (*Micrococcus luteus*), diatom Navicula, and barnacle cyprids. Particularly, marine field tests demonstrate that the polymer has excellent antibiofouling performance in 110 days.



KEYWORDS: *biofouling, low surface energy, poly(dimethylsiloxane), antifoulant, polyurethane*

INTRODUCTION

Marine biofouling due to the undesired settlement of marine organisms such as bacteria, algae, and barnacles on the immersed surface has been a serious problem for maritime industries.[1−4] The most effective approach is to use biocidal coating containing tributyl tin (TBT), but it was banned in 2008 because of its persistent toxicity in aquatic systems.[5,6] In recent years, more attention has been turned toward environmentally friendly materials such as zwitterionic polymers,[7−9] slippery liquid-infused surfaces,[10] hydrolyzable[11−14] and biodegradable polymers,[15−19] microstructured surfaces,[20−22] and low-surface-energy elastomers.[23−26] In principle, low-surface-energy elastomer has weak interaction with fouling organisms, so that the marine biofouling accumulated on the surface can be removed by mechanical cleaning or shearing force of seawater.[27,28] Their antibiofouling ability comes from the low surface energy and low elastic modulus.[29,30] However, such polymers usually suffer from weak adhesion to substrates and poor mechanical strength. Besides, they have limited ability to stop the fouling accumulation, especially during static periods with the formation of slime layer consisting of various bacteria and diatom.[26] To improve the mechanical performance, they were chemically modified with epoxy[31] and polyurea.[32] Unfortunately, such modifications often cause the surface energy or elastic modulus to increase and thus reduce the antifouling efficacy. Zwitterionic groups and quaternary ammonium salts were chemically incorporated into silicone to improve its antifouling performance.[33−38] Yet, the introduction of the hydrophilic groups can make the polymer swollen in marine environment, which reduces its mechanical strength.

As a typical low surface energy elastomer, poly(dimethylsiloxane) (PDMS) has been used for marine antibiofouling.[39,40] However, because of its low modulus (∼1 MPa), it is susceptible to mechanical damage in practical applications.[41,42] PDMS also has a weak adhesion to substrates due to the nonpolar and inert nature.[43] Moreover, it has a poor fouling release efficacy to diatom even under a high pressure from water jet.[41] Accordingly, its antibiofouling performance and mechanical properties need improving. In the present study, we have prepared polyurethane with PDMS as the main chain and *N*-(2,4,6-trichlorophenyl) maleimide (TCM) as pendant groups. TCM is an environment-friendly organic marine antifouling agent with a low toxicity.[18] Here, TCM groups attached to the polymer are expected to kill the contacted marine organisms while the low energy surface facilitates the detachment of adhered biofouling. Because the antifoulant groups are fixed on polymer chains, the polymer surface is expected to have durable antibiofouling ability, and the antifoulants will not be released into the marine and thus have little impact on the environment. We have systematically investigated the surface properties and antibiofouling performance of the polymer by using laboratory and marine field tests.

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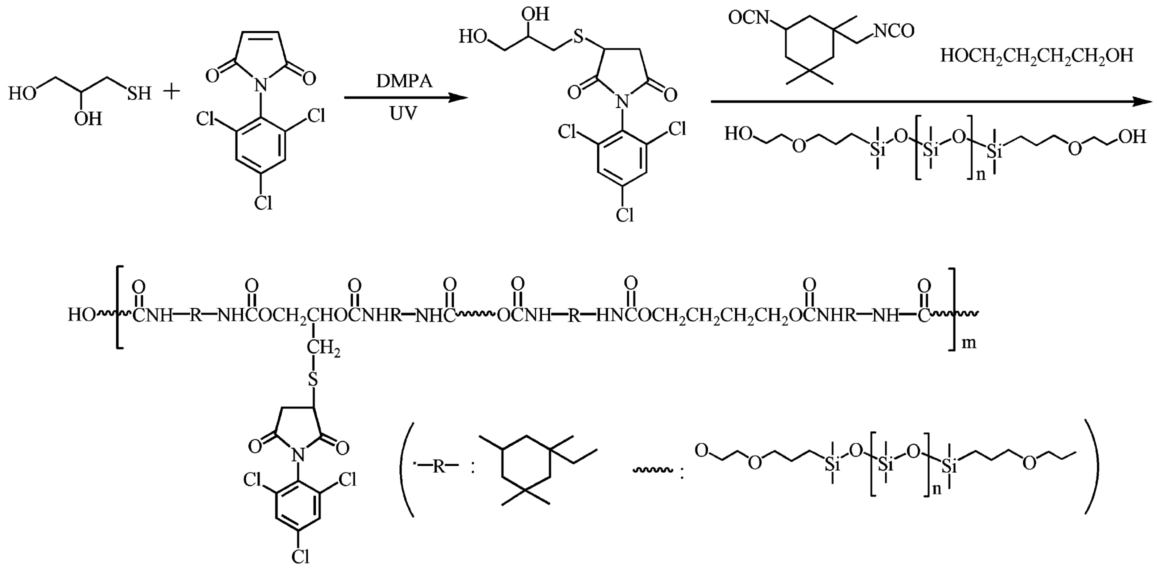
Scheme 1. Synthesis of PDMS−PU-*x* with TCM Pendant Groups



Our aim is to develop effective and environmentally friendly antibiofouling materials used under static conditions.

■ EXPERIMENTAL AND METHODS

Materials. Poly(dimethylsiloxane) diol (PDMS, M_w = 1800 g/mol) was from Shin-Etsu Chem. and dried under reduced pressure for 2 h prior to use. *N*-(2,4,6-trichlorophenyl) maleimide (TCM) from Linsheng Chem. was recrystallized from ethanol twice and dried under reduced pressure at 50 °C overnight. 3-Mercapto-1,2-propanediol (TPG) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were from Aladdin and used as received. 1,4-butane diol (1,4-BD) from Aldrich was dried under reduced pressure for 2 h prior to use. Dibutyltin dilaurate (DBTDL) from Aldrich was used as received. Isophorone diisocyanate (IPDI) from Aladin was used as received. Tetrahydrofuran (THF) was refluxed over CaH_2 and distilled prior to use. PDMS elastomer (Sylgard 184) was purchased from Dow Corning. Artificial seawater was prepared following ASTM D1141−98 (2003). Other reagents were used as received.

Synthesis of PDMS-Based Polyurethane with TCM Pendant Groups. The synthesis and characterization of $TCM(OH)_2$ were detailed elsewhere.[18] PDMS based polyurethane with TCM pendant groups was synthesized via a condensation reaction (Scheme 1). Typically, 1.97 g (8.8 mmol) of IPDI and 6.00 g (3.3 mmol) of PDMS was introduced to a round-bottom flask equipped with a condenser under a nitrogen atmosphere with THF as solvent.[44] The mixture was stirred at 70 °C for 1 h yielding a prepolymer. Subsequently, 2.00 g (5.2 mmol) of $TCM(OH)_2$ was added and the reaction was conducted at 80 °C for 1 h, 0.03 g (0.3 mmol) of 1,4-BD and 0.02 g of DBTDL were added as the chain extender and catalyst, respectively. The mixture was allowed to react at 80 °C for 3 h. Note that the feed weight ratio of the reactants can significantly influence the antibiofouling performance and mechanical properties of the resultant polymer. It was optimized through a number of preliminary experiments. The resulting polymer was precipitated into excessive water, washed three times, and dried under vacuum at 60 °C for 24 h. ^1H NMR (600 MHz, $CDCl_3$, ppm): 0.06 ($OSi(CH_3)_2O$), 0.52 ($CH_2OCH_2CH_2CH_2Si$), 1.61 ($CH_2OCH_2CH_2CH_2Si$), 3.42 ($CH_2OCH_2CH_2CH_2Si$) 3.60 ($COOCH_2CH_2OCH_2$), 3.72 ($COOCH_2CH_2OCH_2$), 1.06 ($CH_2C(CH_3)_2CH_2$), 1.25 ($CH_2CHNHCOO$), 3.79 ($CH_2CHNHCOO$), 2.91 (CH_3CCH_2NHCOO), 4.09 ($OCH_2CH_2CH_2CH_2O$), 1.68 ($OCH_2CH_2CH_2CH_2O$), 7.47 (C_6H_2). IR: 3350 cm^{-1} (NH), 3080 cm^{-1} (C_6H_2), 2960 cm^{-1} (CH_3), 2865 cm^{-1} (CH_2), 1730 cm^{-1} (C=O), 1090 cm^{-1} (Si−O−Si). For convenience, the PDMS-based polyurethane with TCM pendant groups is designated as PDMS−PU-*x*, where *x* is the weight percentage of TCM determined by ^1H NMR. The characterization data are summarized in Table 1 and the details can be found in the Supporting Information.

Table 1. Characterization Data of PDMS−PU-*x*

sample	IPDI/PDMS/ $TCM(OH)_2$ /1,4-BD[a]	TCM content (wt %)[b]	M_n[c]	$Đ_M$[c] (g/mol)	yield (%)
PDMS−PU-0	30.6/60/0/9.4	0	40 000	1.3	94.2
PDMS−PU-7	26.8/60/7/6.2	6.9	22 000	1.4	93.6
PDMS−PU-14	23.0/60/14/3.0	14.1	23 000	1.4	95.1
PDMS−PU-20	19.7/60/20/0.3	20.2	19 000	1.4	92.6

[a] Feed weight ratio. [b] Determined by ^1H NMR. [c] Determined by GPC.

Characterization. *Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR).* All ^1H NMR spectra were recorded on a Bruker AV600 NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The spectra were collected at 64 scans with a spectral resolution of 4 cm^{-1} by a KBr disk method.

Gel Permeation Chromatography (GPC). The number-average molecular weights (M_n) and molecular weight dispersity ($Đ_M$) were determined by GPC at 50 °C on a Waters 1515. A series of monodisperse polystyrenes were used as standard in the fluent of DMF and LiBr with a flow rate of 1.0 mL/min.

Preparation of Polymer Film. Each polymer film with dry thickness of ~300 μm was prepared via a solution-casting. Typically, a polymer solution in THF (30% w/v) was dropped on an epoxy resin panel (for contact angle measurement, adhesion test, surface topography observation, diatom Navicula assay, and marine field test), a glass slide (for antibacterial test and barnacle cyprids settlement assay), or a Teflon mold (for DMA or XPS measurement) and dried at room temperature for 5 days to remove the solvent.

X-ray Photoelectron Spectroscopy (XPS). XPS analysis was conducted on an Axis Ultra DLD (Kratos Analytical) with a monochromate Al Kα ($h\nu$ = 1486.6 eV) source at takeoff angles of 90° under a pressure of 5×10^{-9} Torr. The X-ray gun was operated at the voltage of 15 kV and current of 5 mA. Binding energies were all referenced to the C 1s at 284.6 eV. The mass ratio of Cl/Si is the average in three tests for the same specimen.

Dynamic Mechanical Analysis (DMA). DMA measurements were performed on a Netzsch DMA 242 in tensile mode. The samples (8 mm long, 6 mm wide, and 0.5 mm thick) were analyzed from −130 to 60 °C at a frequency of 1 Hz.

Contact Angle Measurements. The static contact angle measurements were conducted on a Contact Angle System OCA40 (Dataphysics) by placing 3 μL liquid droplets on the sample surfaces using the sessile method. Contact angles of deionized water and diiodomethane were measured at 25 °C. Five different regions of each sample were measured to obtain an average value. The surface energy of the polymer was calculated with the built-in OCA40 software from water and diiodomethane contact angles using the Owens−Wendt−Rabel−Kaelble method.[45]

Surface Roughness Measurements. The surface roughness measurement and topography observation of PDMS−PU-*x* film were conducted on a BMT Expert 3D surface profile measurement system. For each film, eight line-scan measurements in the range of 2 mm were performed to obtain an average value of the average surface roughness (Ra).[26] Area-scan measurements (0.5 × 0.5 mm^2) were conducted to study the surface topography. The profile of surface is reflected from the difference in color. The cutoff length used is 0.8 mm.

Adhesion Tests. The pull-off strength (adhesion) of PDMS−PU-x film to the glass fiber reinforced epoxy resin panel was measured using pull-off adhesion tester (PosiTest AT-A Automatic) according to ASTM D4541−09.[46] The measurement area is 20 mm in diameter and the pull rate was set at 0.2 MPa/s. Five different points on each sample were tested to obtain an average value.

Antibacterial Assays. Marine bacteria *Micrococcus luteus* (M. luteus) was used to evaluate the antibacterial adhesion of PDMS−PU-*x* since it is widespread in South China Sea where our field tests were conducted. Concentration of bacteria suspension was determined by counting bacterial cell under optical microscope (Scope. A1; Zeiss, Germany). Bacteria were diluted with artificial seawater at a concentration of 1 × 10^8 cells/mL. Each substrate coated with PDMS−PU-*x* was then immersed in 1.0 mL of bacterial suspension under static condition at 37 °C for 12 h. The adhered bacterial cells on the surface of PDMS−PU-x were fixed with 3% of glutaraldehyde. Each sample was sputter-coated with gold to minimize sample-charging and investigated under Quanta 200 scanning electron microscope (SEM, Philips-FEI Corporation, Netherlands) operating at 10.00 kV.

Diatom Navicula Colonization Assays. Marine diatom Navicula was cultured using a procedure reported before.[38] Navicula cell suspension was placed on the polymer surface at 25 °C with illumination. After 14 days, the surface was rinsed with seawater to remove the unattached diatoms and observed under a microscopy.

Barnacle Cyprids Settlement Assays. Cyprids of B. amphitrite were incubated following a procedure reported before.[47,48] Typically, 1.0 mL of filtered seawater containing about 30 cyprids was dropped on the sample surface. After incubation in darkness for 48 h, the cyprids were count using a microscope. The settlement fraction is defined as the ratio of the number of settled cyprids to that of the total cyprids. Three specimen were tested for each polymer sample.

Marine Field Tests. The field tests were performed from September 2014 to January 2015 in South China Sea (22°33′N, 114°31′E), where the temperature of surface water ranges from 25 to 28 °C and the salinity is 35 ‰. The diversified biofouling occurs at all seasons, and the biofouling pressure mainly comes from bacteria, crustacea, anneliada, mollusca, bryozoa and algae.[49] The polymer was coated on the glass fiber reinforced epoxy resin panels (100 × 100 × 3 mm^3) and immersed in seawater at a depth of 1 m. After a certain period of time, the panels were taken out of the sea and carefully washed with seawater and photographed. Then, they were immediately placed into the seawater to continue the test. Glass fiber reinforced epoxy resin panels as a control sample and panels coated with PDMS−PU-*x* were tested.

RESULTS AND DISCUSSION

As shown in Table 1, ^{1}H NMR, FTIR, and GPC measurements demonstrate we have successfully synthesized polyurethane (PDMS−PU-*x*) with PDMS main chains and TCM pendant groups. Its average molecular weight (M_n) and molecular weight dispersity ($Đ_M$) are 19 000−40 000 g/mol and 1.3−1.4, respectively. The yield is greater than 90%. We first studied the surface energy of the polymer. Figure 1 shows PDMS−PU-*x* has surface energy ranging from 24 to 26 mJ m^{-2}. This is understandable because PDMS−PU-*x* contains 60 wt % PDMS with low surface energy, and it tends to stay at the surface.[50] Note the dispersive component is the vast majority, whereas the polar component is the minor, which is attributed to the nonpolar nature of PDMS. It is known that fouling organisms have weak adhesion to polymer with surface energy of 20−30 mJ m^{-2}.[51] The low surface energy of PDMS−PU-*x* is conducive to the removal of biofouling.

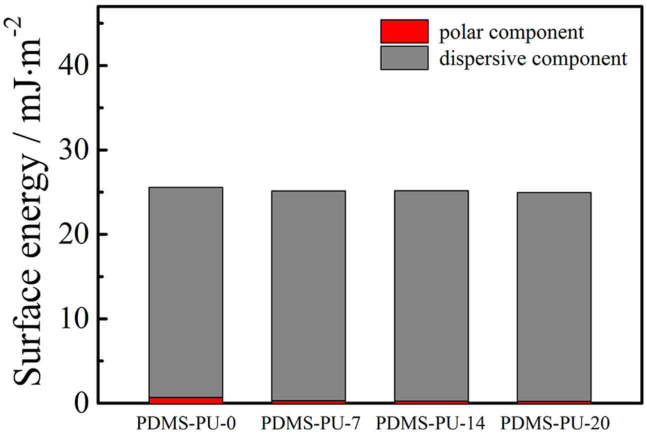


Figure 1. Surface energy of PDMS−PU-x estimated from water and diiodomethane contact angles at 25 °C.

We studied the water contact angle of PDMS−PU-*x* surface immersed in artificial seawater as a function of time (Figure 2). Generally, the water contact angle has a small drop after the immersion. Similar phenomena were reported on some other silicone based polymer.[34,52] This is because the polymer chains are flexible and the hydrophilic -NH groups migrate onto the surface with the rearrangement of polymer chains. Yet, because

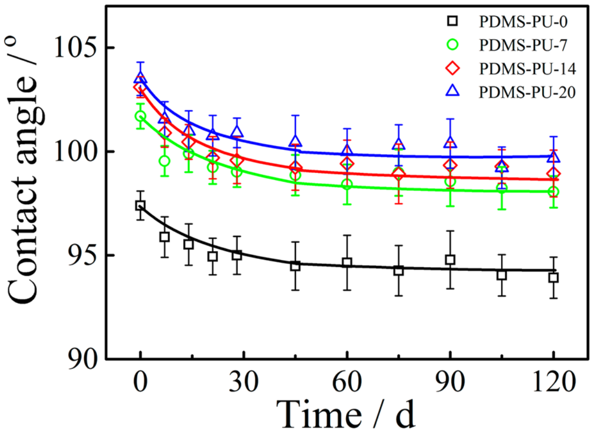


Figure 2. Time dependence of water contact angle of PDMS−PU-x immersed in artificial seawater at 25 °C.

of the limited chain rearrangement, the decrease in contact angle is small. The contact angle levels off after a certain time because the rearrangement of the polymer chains is done. Note that the presence of antifoulants somewhat increases the contact angle because the phenyl in antifoulant group is hydrophobic.

The storage modulus of PDMS−PU-x together with that of pure PDMS elastomer was measured by DMA in tensile mode (Figure 3). Clearly, PDMS−PU-*x* with hard segments has a larger modulus than PDMS elastomer. Also, the modulus of PDMS−PU-*x* increases with the antifoulant content in that the phenyls in antifoulants make the polymer chains more rigid. It is generally recognized that a lower modulus can lead to better fouling release performance.[29,30] The relatively high modulus of PDMS−PU-*x* is not favorable to the fouling removal. However, as shown below, because it has low energy surface and chemically attached antifoulant groups, it still exhibits good antibiofouling performance. Moreover, PDMS−PU-*x* with higher modulus has improved mechanical strength.

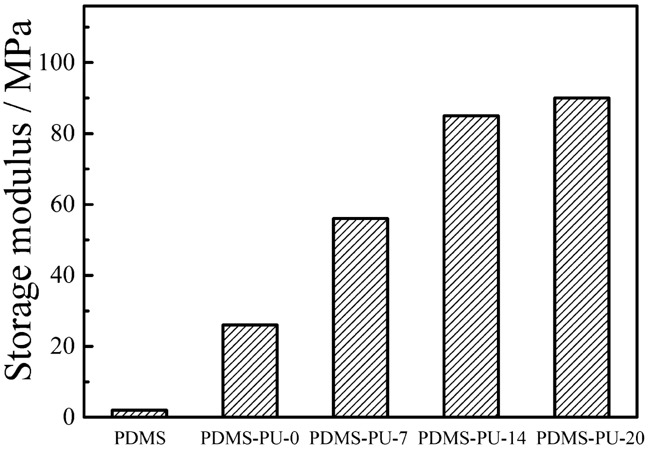


Figure 3. Storage moduli of PDMS−PU-x and PDMS elastomer at 25 °C.

The antifoulant groups on PDMS−PU-*x* surface are critical for its antibiofouling performance. If they are completely covered by PDMS segments, the antibiofouling ability would decline. Table 2 shows the mass ratio of Cl to Si (Cl/Si) in PDMS−PU-*x* estimated from XPS and ^{1}H NMR. Certainly, no Cl is observed in PDMS−PU-0 because it does not contain any antifoulant groups. For any other samples, the mass ratio (Cl/Si) from XPS is lower than that from ^{1}H NMR, indicating that the antifoulant concentration at the surface is lower than that in the bulk. This is because PDMS segments with low surface energy have a strong tendency to migrate to surface and cover some antifoulant groups. Nevertheless, as shown below, when TCM content is above 14 wt %, antifoulant groups exposed on the surface are sufficient for antifouling. Note that the mass ratio (Cl/Si) only slightly varies after the polymer is immersed in artificial seawater for 140 days. This is consistent with the results about contact angle measurements.

Table 2. Mass Ratio of Cl/Si in PDMS−PU-*x*

sample	Cl/Si from ^{1}H NMR[a]	Cl/Si from XPS[a]	Cl/Si from XPS[b]
PDMS−PU-0	0	0	0
PDMS−PU-7	0.083	0.007 ± 0.006	0.008 ± 0.006
PDMS−PU-14	0.172	0.039 ± 0.013	0.035 ± 0.014
PDMS−PU-20	0.234	0.055 ± 0.011	0.061 ± 0.010

[a] Before immersion in artificial seawater. [b] After a 140 days immersion.

We measured the adhesion of the polymer to a substrate. Figure 4 shows the adhesion (pull-off strength) of PDMS−PU-*x* on glass fiber reinforced epoxy resin panels. The adhesion of PDMS−PU-0 is about 1.4 MPa. As the antifoulant content increases, the adhesion gradually decreases. This is because the urethane content in the polymer decreases as the antifoulant content increases and the hydrogen bonding density decreases, leading the adhesion to decrease.[53] Anyhow, PDMS−PU-*x* samples exhibit adhesion above 1.0 MPa, which is enough for the application in marine environment.[31]

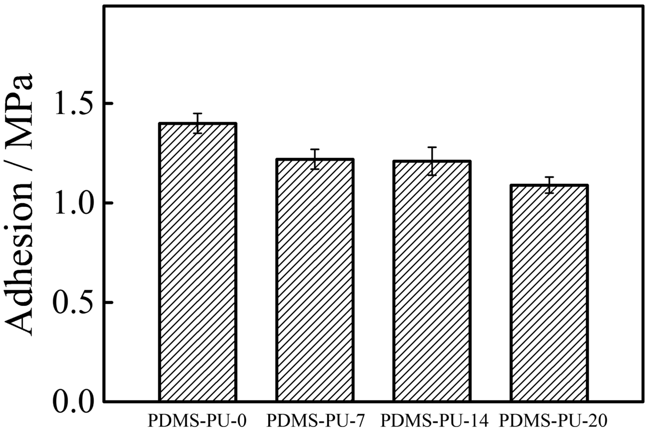


Figure 4. Adhesion strength of PDMS−PU-x on epoxy panel.

The antibacterial efficacy of PDMS−PU-*x* was evaluated against marine bacteria (M. luteus), where PDMS−PU-*x* film was exposed to bacteria suspension (1×10^8 cells/mL) for 12 h. The antibacterial performance was qualitatively analyzed by observing the sample surface under SEM (Figure 5). For PDMS−PU-0, a large number of bacterial cells can be observed at the surface, indicating that the polymer is susceptible to bacterial adhesion and colonization despite its low surface energy. As the antifoulant content increases, the number of adhered bacterial cells decreases. Namely, the introduction of organic antifoulant significantly improves the antibacterial performance of the polymer with low surface energy. Note that surface smoothness can influence the settlement and removal of marine organisms.[54,55] Our studies show that PDMS−PU-*x* has small roughness (Ra $\lesssim$ 0.3 μm) in artificial seawater and the surface topography slightly varies with time (Figures S6 and S7). Thus, we do not consider the effect of surface topography on the antibiofouling performance here.

Marine diatom Navicula was also used to evaluate the antifouling ability of PDMS−PU-x (Figure 6). After 14 days of incubation, a great amount of Navicula have colonized and grown on the surface of PDMS−PU-0. It is recognized that hydrophobic surfaces have limited effect on the formation of diatom.[26,41] Therefore, it is not surprising that PDMS−PU-0 has a low efficacy to Navicula because it is hydrophobic and does not contain any antifoulant groups. As TCM content increases, a remarkable reduction of Navicula can be observed on PDMS−PU-*x* surface including PDMS−PU-7 with limited antifoulant on surface. Accordingly, the chemically attached antifoulants play critical role in inhibiting the fouling from diatom.

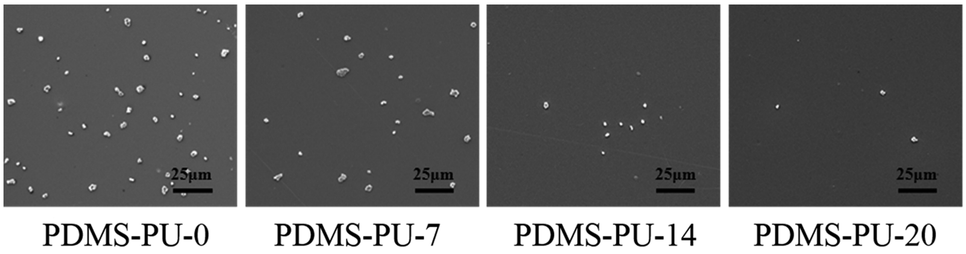


Figure 5. SEM images of PDMS−PU-*x* after exposure to M. luteus (1×10^8 cells/mL) for 12 h.

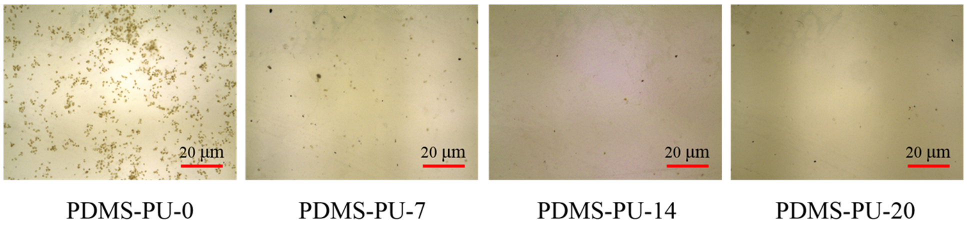


Figure 6. Surfaces of PDMS−PU-*x* after exposure to diatom Navicula for 14 days.

Figure 7 shows the settlement fraction of barnacle cyprids on PDMS−PU-*x* surface after an incubation of 48 h. About 60% of barnacle cyprids settle on PDMS−PU-0 surface. However, the settlement fraction dramatically decreases as the antifoulant content increases. For PDMS−PU-14 and PDMS−PU-20, the settlement fraction is only about 5%. Moreover, a high mortality rate of barnacle cyprids is observed on PDMS−PU-14 and PDMS−PU-20 surfaces. Such phenomenon does not happen on PDMS−PU-0 or PDMS−PU-7 surface. Clearly, PDMS−PU-*x* with antifoulant content above 14 wt % has high antifouling efficacy against barnacle cyprids. Besides, we examined the artificial seawater in which PDMS−PU-20 had been immersed for 70 days by using liquid chromatography−mass spectrometer (data not shown), and we did not find any TCM residue. In brief, TCM groups conjugated by thioether bonds act as contact killer.

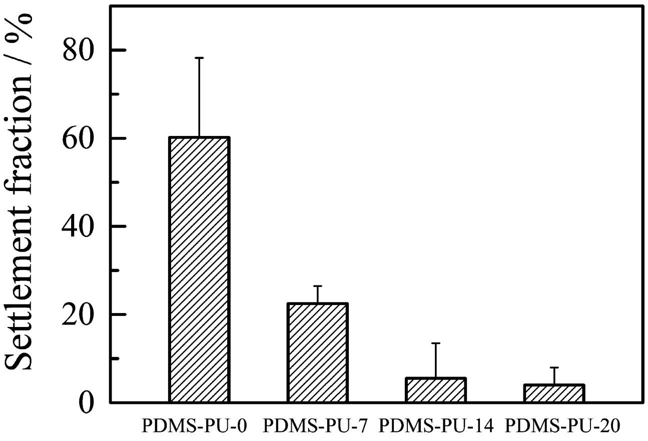


Figure 7. Settlement fraction of barnacle cyprids on the surface of PDMS−PU-*x* after incubation for 48 h.

The antifouling performance of polymer was usually evaluated by laboratory test using marine organisms in the past. However, such conditions are quite different from those in marine environment. Here, the marine antibiofouling ability of PDMS−PU-x was examined by field tests in South China Sea (Figure 8). After immersion in seawater for 30 days, the control panel with epoxy surfaces was seriously fouled by algae, calcarina and bryozoans, indicating a heavy fouling pressure in

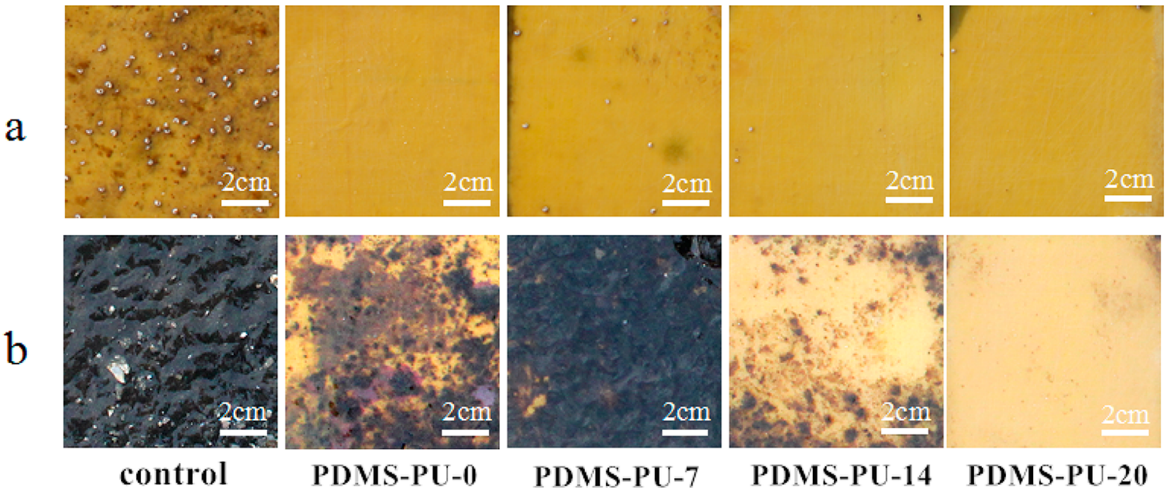


Figure 8. Images of panels coated with PDMS−PU-*x* after immersion in South China Sea for (a) 30 days and (b) 110 days.

the testing site. Meanwhile, almost no biofouling can be observed on panels coated with PDMS−PU-*x*. Note that PDMS−PU-0 also shows good antibiofouling performance in 30 days. This is because it has low surface energy and thus a weak interaction with organisms. After 110 days, PDMS−PU-0 is already fouled but it shows better antibiofouling performance than PDMS−PU-7. This is because PDMS−PU-7 has a higher modulus though it has surface energy slightly lower than PDMS−PU-0. Moreover, the antifoulant content is limited in PDMS−PU-7, so it has an even poorer performance than PDMS−PU-0. Yet, PDMS−PU-14 and PDMS−PU-20 exhibit excellent antibiofouling performance with few organisms colonized after 110 days. Considering that they have higher modulus than PDMS−PU-0 and PDMS−PU-7, the presence of the attached antifoulants and their low surface energy are responsible for their antibiofouling performance. Note that we only examined the antifouling performance of the polymers under static conditions. The polymers are expected to exhibit better performance with the help of shear force under dynamic conditions. We will test it in the future. Anyhow, the marine field tests demonstrate that the polymer is promising to find maritime applications.

Figure 9 illustrates the antifouling mechanism of PDMS−PU-*x*. The attached antifoulants (TCM) act as contact killer. PDMS segments with low surface energy facilitate the removal of biofouling. Their cooperation gives rise to the good antibiofouling performance of the polymer.

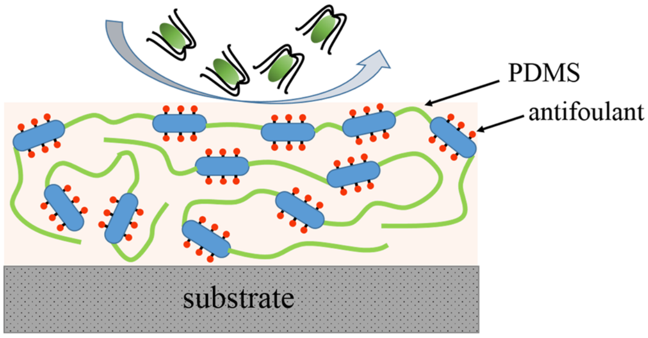


Figure 9. Antifouling mechanism of PDMS−PU-*x*.

CONCLUSION

We have prepared poly(dimethylsiloxane) (PDMS)-based polyurethane with antifoulant pendant groups by a combination of a thiol−ene click reaction and a condensation reaction. Our studies show that the polymer has low surface energy and a stably smooth surface in artificial seawater. The polymer exhibits good mechanical properties with sufficiently high storage modulus and adhesion to substrate. The polymer with chemically attached antifoulants exhibits high antifouling efficacy against various marine organisms. Particularly, marine field tests demonstrate the polymer has good marine antibiofouling performance. The combination of material with low surface energy and chemically attached antifoulants provides an eco-friendly strategy to battle marine biofouling.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07325.

^{1}H NMR, GPC, and FTIR spectra on the synthesis of PDMS−PU-*x*, XPS spectra, time dependence of surface roughness, and temperature dependence of storage modulus of PDMS−PU-*x* (PDF)

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Notes

The authors declare no competing financial interest.

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