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Environmentally Friendly Antifouling Coatings Based on Biodegradable Polymer and Natural Antifoulant

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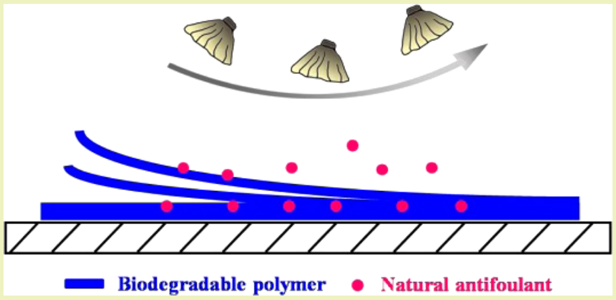
Supporting Information



ABSTRACT: Marine biofouling causes huge economic losses and serious problems to maritime industries. Consequently, there is a great demand for environmentally friendly antibiofouling technology. In the present study, we developed novel antifouling coatings by incorporating butenolide derived from marine bacteria into biodegradable poly(ε-caprolactone) based polyurethane. Measurements of mass loss indicated that the polymer was degraded in seawater and that the degradation rate increased in the presence of marine organisms or enzymes. Moreover, measured release rates indicated that butenolide could be released from the biodegradable polymer for at least 3 months and the release rate depended on both the concentration of butenolide and the temperature. Incorporating a naturally occurring resin (rosin) into the biodegradable polymer increased the self-renewal rate and improved the later release rate of butenolide. The field test indicated that the system had excellent antifouling properties.

KEYWORDS: *Biodegradable polyurethane, Poly(ε-caprolactone), Butenolide, Rosin, Controlled release, Antifouling coating*

INTRODUCTION

Marine biofouling, arising from the undesirable accumulation of marine microorganisms, plants, and animals on submerged surfaces, causes huge economic losses and serious problems to maritime industries.[1−3] It is generally agreed that the most effective and convenient method of preventing marine fouling is achieved by coatings which release toxic molecules at a controlled rate to inhibit the growth of adhered organisms such as bacteria, algae, and mollusks.[4,5] Tributyltin (TBT) or copper based coatings are effective, but they have a negative impact on the environment.[6] Therefore, there is an urgent need to develop environmentally friendly, nontoxic, or low-toxicity antifouling (AF) compounds.[7,8]

Natural products isolated from marine microorganisms, seaweeds and aquatic plants, marine invertebrates, and terrestrial and other sources are a promising source of antifouling biocides. They have the advantage of compatibility with biological systems and are more specific than heavy metals.[9−11] However, although numerous potential antifouling compounds have been isolated from marine natural products, progress in applying them as effective antifouling agents has been slow. We still face practical challenges, such as the cost-effective mass production of compounds, biosafety, and antifouling mechanisms. Furthermore, addressing the incorporation of antifouling compounds into polymers and the compatibility and controlled release of natural antifoulants from coatings are equally important issues.[12]

Our group recently discovered an ecologically benign antifoulant, 5-octylfuran-2(5*H*)-one (known as butenolide), derived from marine bacteria *Streptomyces* spp. and showing strong antifouling activity by preventing the larval settlement of major fouling species, such as barnacles and bryozoans.[13] Moreover, the fast degradation, low toxicity against nontarget organisms, and simple structure of the synthetic butenolide make it a promising antifouling compound with a large potential market.[14−17] However, the previous works generally focus on the property of butenolide itself; the compatibility with polymer and controlled release of butenolide from coatings are still urgent and unsolved problems.

In the present study, we developed environmentally friendly antifouling coatings based on biodegradable polymers and natural products. Degradation of the polymer provides a self-renewing surface and serves as both carrier and release system of butenolide. Particularly, with the polyester main chains, they can degrade due to the hydrolysis of ester linkage and enzymatic attack by microorganisms in marine environment, quite different from the traditional self-polishing copolymers with nondegradable hydrocarbon main chains which lead to ecological harm.[18−21] We have investigated polymer degradation, the release of butenolide, and its antibiofouling perform-

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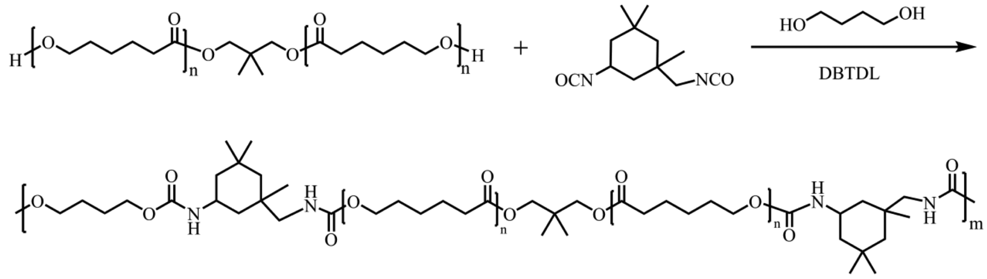
Scheme 1. Synthesis of PCL-Based Polyurethane



ance, allowing the development of high performance marine antifouling systems based on natural products.

EXPERIMENTAL SECTION

Materials. Poly(ε-caprolactone) diol (PCL; M_w = 2000 g/mol) acquired from Perstorp, 1,4-butanediol (BDO) and dibutyltin dilaurate (DBTDL) from Aldrich, and isophorone diisocyanate (IPDI) from Aladdin were used as received. Rosin was obtained from Wuzhou Sun Shine Forestry & Chemicals Co., Ltd., of Guangxi (China). The PCL was dried under reduced pressure for 2 h prior to use. Tetrahydrofuran (THF) was refluxed over CaH_2 and distilled prior to use. Butenolide with a purity of >99% was synthesized by ChemPartner (Shanghai). Artificial seawater (ASW) was prepared according to ASTM D1141-98(2013).[22] Natural seawater (NSW, salinity, 33‰; pH 8.17) was collected from the subtidal zone in Port Shelter, Hong Kong (22°20′16.7″N, 114°16′08.0″E). The other chemical agents used in this study were of analytical grade.

Synthesis of PCL-Based Polyurethane (PCL−PU80). PCL-based polyurethane was synthesized by polyaddition (Scheme 1). First, IPDI reacted with PCL diol at 70 °C for 1 h in THF under a nitrogen atmosphere, yielding a prepolymer. Subsequently, 1,4-BD and DBTDL were added as the chain extender and catalyst respectively, and the mixture was allowed to react at 80 °C for 3 h. The product was precipitated into hexane twice, filtered, and dried under vacuum at 40 °C for 24 h. ^1H NMR (400 MHz, $CDCl_3$, ppm): 4.05 ($COCH_2CH_2CH_2CH_2\mathit{CH_2}O$), 2.30 ($CO\mathit{CH_2}CH_2CH_2CH_2CH_2O$), 1.65 ($COCH_2\mathit{CH_2}CH_2\mathit{CH_2}CH_2O$), 1.38 ($COCH_2CH_2\mathit{CH_2}CH_2CH_2O$), 3.68 ($O\mathit{CH_2}CH_2CH_2\mathit{CH_2}O$), 1.63 ($OCH_2\mathit{CH_2}\mathit{CH_2}CH_2O$), 3.80 ($CH_2\mathit{CH}(CH_2)NHCO$), 2.91 ($OCNHC\mathit{H_2}C(CH_2)_2CH_3$), 1.06 ($OCNHCH_2C(CH_2)_2\mathit{CH_3}$). IR: 3360 cm^{-1} (NH), 2950 cm^{-1} (CH_3), 2860 cm^{-1} (CH_2), 1730 cm^{-1} (C═O). The M_n and polysispersity index (PDI) are 2.7× 10^4 g/mol and 1.87, respectively. The details can be found in Figures S1−S3.

Preparation of Biodegradable Polymer/Butenolide Coatings. The coating was prepared by mixing solutions. Typically, PCL−PU80 (0.95 g, 95 wt %) and butenolide (0.05 g, 5 wt %) were dissolved by vigorous stirring in xylene at 25 °C. Then the solution was coated on a substrate and dried at room temperature for 7 days to remove the solvent. Other coatings with different contents of butenolide were prepared using the same procedure. The dry thickness of each coating is ∼400 μm. For the PCL−PU80/rosin composites, the weight ratio is 6/10.

Hydrolytic Degradation. The hydrolytic degradation test was conducted in ASW and NSW at 25 °C. The composite film was prepared on an epoxy resin panel (20 × 20 mm^2) using the solution-casting method. The weighed sample (W_0) of each dried coating together with its panel was incubated in a tank of ASW or NSW that was renewed every 2 weeks. After a period of time, the panel was taken out, rinsed with deionized water three times, and dried in a vacuum freeze-dryer until the weight (W_t) remained constant. The mass loss was estimated using the equation:

$$\text{mass loss (g)} = W_0 - W_t \tag{1}$$

For each sample, three coated panels were prepared and measured, and each data point was averaged over three successive, consistent measurements.

Enzymatic Degradation. Enzyme degradation experiments were performed on an E1 quartz crystal microbalance with dissipation (QCM-D) from Q-Sense AB. The details can be found elsewhere.[23,24] QCM-D simultaneously monitors changes in resonance frequency (Δf) and dissipation (ΔD) in real time. Δf is related to changes in the mass attached to the oscillating sensor surface, whereas ΔD relates to the viscoelasticity of the adsorbed layer. Lipase PS solution (0−1.0 mg/mL) was delivered to the surface at a flow rate of 150 μL/min, and artificial seawater was used as the reference. The changes in frequency (Δf) and dissipation (ΔD) reflect information about the mass and structural changes of the film. Increases in the oscillation frequency indicate the mass loss of the film on the QCM sensor surface. All the data used were from the third overtone (n = 3). Δf and ΔD values from the fundamental were discarded because they were usually noisy due to insufficient energy trapping.[25] All the experiments were conducted at 25 °C.

Determination of the Release Rate of Butenolide. The release rate of butenolide was determined by measuring its concentration using high performance liquid chromatography (HPLC) under a static condition.[16,26] Typically, a composite film was prepared on an epoxy resin panel (20 × 70 mm^2), and then the panel was immersed in artificial seawater (ASW). After a given period of time, the panel was transferred from the holding tank to an individual measuring container with 100 mL of fresh seawater. After 24 h immersion, 10 mL of seawater was taken from the individual measuring container and extracted three times using 10 mL of dichloromethane. After drying under nitrogen gas, the extract was resuspended in 100 μL of 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 butenolide peaks were determined from the retention time, and its amount was calculated from the established standard curves using peak areas plotted against known quantities of standards. The recovery efficiency for butenolide analysis is 87.7%.

Marine Field Tests. The field tests were performed from July to October 2016 on a fish farm at Yung Shue O, Hong Kong (114°21′E, 22°24′N), where the rafts are fouled heavily almost year around. The samples applied to PVC panels (15 × 20 cm^2) were lowered into seawater at a depth of 0.5 m. After a certain period of time, the panels were taken out of the sea, washed with seawater to remove the sea mud and photographed, and then placed back in the sea to continue the test. All the panels were washed similarly so that we can account for the deposition of sea organisms on the panel to compare the antifouling ability.

RESULTS AND DISCUSSION

Figure 1 shows the time dependence of mass loss of the PCL−PU80 in artificial seawater (ASW) and natural seawater (NSW). After immersion for 3 days, each film started to lose weight, indicating hydrolytic degradation. Moreover, the hydrolytic degradation rate increased when the PCL−PU80 was immersed in NSW. In particular, the polymer had a higher mass loss in NSW. Various microorganisms such as bacteria, actinomycetes, and fungi in natural marine environments are reported to secrete enzymes which induce biodegradation of

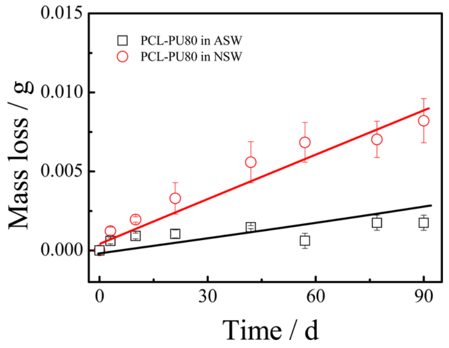


Figure 1. Time dependence of mass loss of PCL−PU80 in artificial seawater and natural seawater at 25 °C.

ester-containing polymers.[27−31] The higher mass loss of PCL−PU80 in NSW might be attributed to the enzymatic degradation.

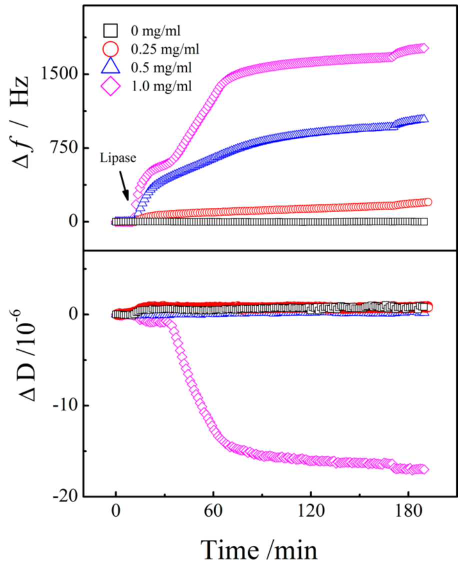


Figure 2. Time dependence of frequency shift (Δ*f*) and energy dissipation shift (Δ*D*) for enzymatic degradation of PCL−PU80 in artificial seawater at 25 °C.

To understand the enzymatic degradation of PCL−PU80 in marine environment, we examined the degradation of the polymer in the presence of lipase PS. Figure 2 shows the time dependence of the frequency shift (Δ*f*) and the energy dissipation shift (Δ*D*) for the enzymatic degradation of PCL−PU80. For PCL−PU80, as lipase PS was introduced, Δ*f* increased and gradually leveled off. After rinsing with seawater, Δ*f* increased markedly relative to the baseline, showing that the mass of the film decreases. In other words, PCL−PU80 film degraded into small molecules and dispersed in ASW. Moreover, the frequency shift increased as the content of lipase PS changed from 0 to 1.0 mg/mL, indicating that the degradation rate increased with lipase PS content. On the other hand, when the content of lipase PS was below 0.5 mg/mL, Δ*D* increased and gradually leveled off. After rinsing with seawater, Δ*D* had a slight increase relative to the baseline, indicating nonuniform degradation. As the content of lipase PS increased to 1.0 mg/mL, Δ*D* decreased with time. As we know, Δ*D* increased with structural change but decreased with mass loss of the film. The Δ*D* decreased because the contribution of enzymatic degradation to Δ*D* was larger than that of nonuniform structure.[32] The observation indicates that the degradation rate or self-renewal ability was sensitive to the content of lipase secreted by marine microorganisms and a potential system for fouling pressure-sensitive antifouling coatings.

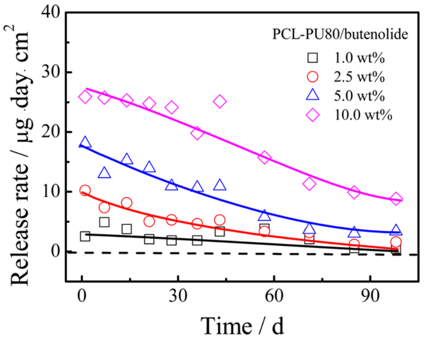


Figure 3. Time dependence of release rate of butenolide from biodegradable PCL−PU80.

The controlled release of antifoulants determined the duration and antifouling performance of an antibiofouling system. Figure 3 shows the time dependent release rate of butenolide at different concentrations. For either PCL−PU80/butenolide, the release rate was time dependent. Over a month, the release rates were constant and higher than 10 μg day^{-1} cm^{-2} for PCL−PU80/butenolide with concentrations of 5.0 and 10.0 wt %. As time increased, the release rate decreased. This was probably because the slow degradation rate of PCL−PU80 did not support constant release of the butenolide over a long period. On the other hand, the release rates varied with the concentration of butenolide and were positively correlated with the butenolide concentration in PCL−PU80. In other words, the rate of release could be changed by adjusting the concentration of butenolide.

To improve the long-term release rate, we added rosin to PCL−PU80. Rosin is a naturally occurring resin extracted from trees. It is soluble in seawater and is the most common raw material in antifouling coatings. Figure 4a shows the mass loss of PCL−PU80/rosin composited with a ratio of 6:10. Compared with PCL−PU80, the mass loss increased when we introduced rosin into PCL−PU80. Figure 4b shows the release rate of butenolide (5.0 wt %) from PCL−PU80 and PCL−PU80/rosin. Compared with that of PCL−PU80, the initial release rate of butenolide from PCL−PU80/rosin decreased but the long-term release rate increased. As discussed above, the degradation rate of PCL−PU80 was very slow, which led to decreased release of butenolide after a period of time. Rosin could increase the self-polishing rate and improve the late release of butenolide from biodegradable polymer.

Considering the diverse temperature of marine environments, we also examined the release of butenolide from PCL−PU80 and PCL−PU80/rosin as a function of temperature (Figure 5). For PCL−PU80, all the samples had a high initial release rate. However, the release rate decreased with time even when the temperature was raised from 20 to 30 °C. For the PCL−PU80/rosin, the initial release rate decreased but the long-term release rate did not decrease much as that of PCL−PU80. Therefore, the release of butenolide was temperature-dependent and the release rate increased as the temperature increased from 20 to 30 °C. This was understandable

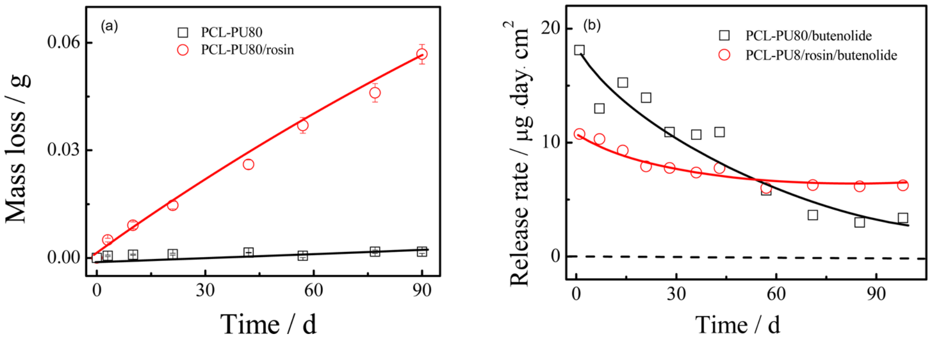


Figure 4. Time dependent mass loss of PCL−PU80 and PCL−PU80/rosin in ASW (a), and release rate of butenolide from PCL−PU80 and PCL−PU80/rosin (b).

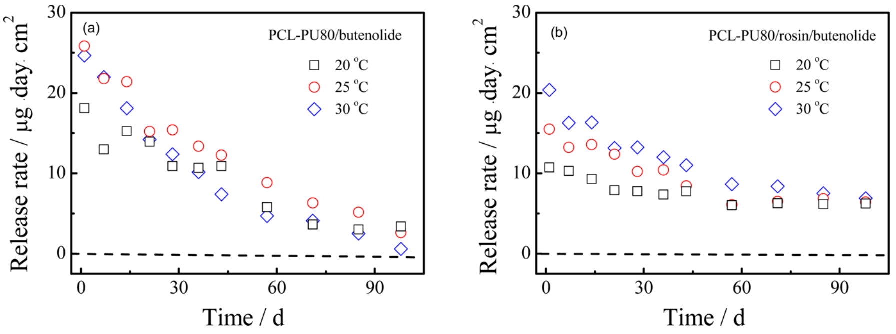


Figure 5. Temperature dependence release rate of butenolide from PCL−PU80 (a) and PCL−PU80/rosin (b).

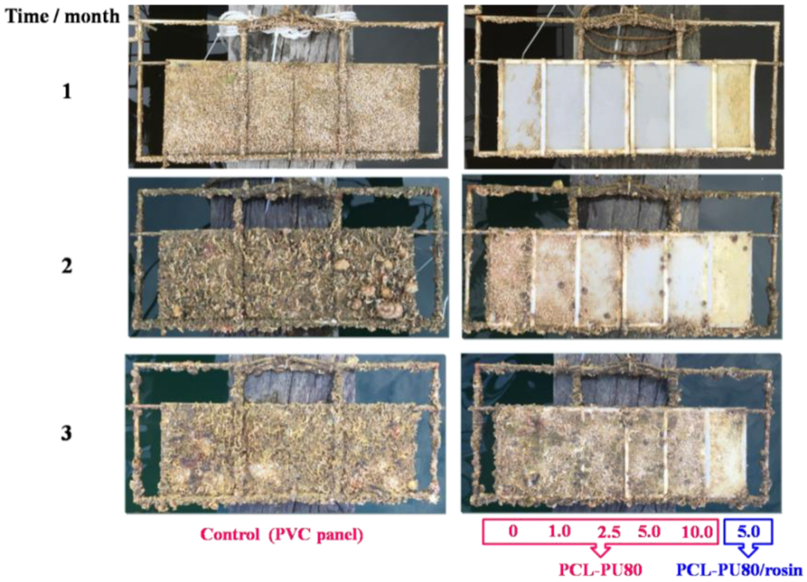


Figure 6. Field test of PCL−PU80/butenolide and PCL−PU80/rosin/butenolide coatings after 3 months.

considering that the melting point of butenolide is 23 °C. Thus, movement of butenolide in the polymer matrix became easier and the release rate increased.

The short-term antifouling performance of the coatings was evaluated by field tests at sea. Figure 6 shows typical images of panels coated with the PCL−PU80/butenolide and PCL−PU80/rosin/butenolide after immersion in seawater for 3 months. After 1 month, the control PVC panel was seriously fouled by marine organisms, indicating a high fouling regime. All the samples coated with PCL−PU80/butenolide or PCL−PU80/rosin/butenolide had good antifouling ability except for the PCL−PU80, indicating the strong antifouling activity of butenolide. After 2 months, fouling on the coated surface decreased as the content of butenolide in the PCL−PU80 increased, indicating that the antifouling efficiency increased. As discussed above, as the content of butenolide increased, the release rate of butenolide increased, so that the antifouling performance was improved. After 3 months, PCL−PU80/rosin exhibited the best antifouling performance. Note that PCL−PU80 with butenolide of 10.0 wt % and PCL−PU80/rosin with butenolide of 5.0 wt % had similar release rates, but their antifouling performances differed. As stated before,[18−21] the antifouling performance is determined by both the self-renewal of the coating and the release of antifoulants. Here, the former also contributed to the antifouling performance in addition to the release of butenolide. Therefore, the surface self-renewal ability is also important for this system as the rosin increased the self-polishing rate and improved the late release of butenolide.

CONCLUSION

We have prepared novel antifouling coatings consisting of biodegradable polymer and butenolide, where butenolide is derived from marine bacteria. The polymer degrades in seawater, and the degradation rate increases in the presence of marine organisms or enzymes. Furthermore, the butenolide can be released from the biodegradable polymer for at least 3 months with the release rate depending on the concentration of butenolide and the temperature. Rosin can increase the self-polishing rate and improve the late release of butenolide. Overall, this system has excellent antifouling ability lasting for more than 3 months.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01385.

^{1}H NMR, FTIR spectra, and GPC chromatograms of PCL-based polyurethane (PDF)

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Notes

The authors declare no competing financial interest.

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