

Rapid Communication

ANTI-BIOFOULING BY DEGRADATION OF POLYMERS^{*}

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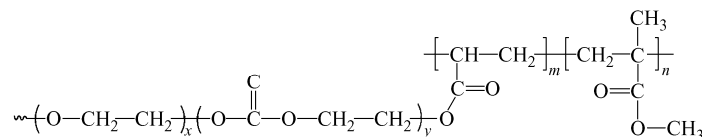
Abstract Copolymers of methyl methacrylate (MMA) and acrylate terminated poly(ethylene oxide-*co*-ethylene carbonate) (PEOC) macromonomer (PEOCA) were synthesized, and the degradation of the polymers was investigated by use of quartz crystal microbalance with dissipation (QCM-D). It is shown that the polymeric surface exhibits degradation in seawater depending on the content of the side chains. Field tests in seawater show that the surface constructed by the copolymer can effectively inhibit marine biofouling because it can be self-renewed due to degradation of the copolymer.

Keywords: Anti-biofouling; Degradation; Poly(ethylene carbonate); Poly(ethylene oxide).

INTRODUCTION

Marine biofouling occurs worldwide and is a sticky problem for maritime industries^[1–3]. Biocidal coatings containing tributyltin (TBT) formulations had been the primary strategy for anti-biofouling before the global ban on its use. Today, most antifouling coatings are based on cuprous oxide in combination with booster biocides, which are also ecologically harmful^[4, 5]. Thus, environment-friendly antifouling materials including low surface energy elastomers^[6–8], bioinspired engineered topographies^[9, 10], amphiphilic nanostructured coatings^[11–15] and enzymes^[16, 17] have been studied. So far, only a few of the materials have been evaluated at sea by field tests^[3].

In the present study, we have prepared a set of copolymers of methyl methacrylate (MMA) and acrylate terminated poly(ethylene oxide-*co*-ethylene carbonate) (PEOC) macromonomer (PEOCA) (Scheme 1). Studies by quartz crystal microbalance with dissipation (QCM-D) demonstrate that the polymers are degradable in natural seawater. We have examined the anti-biofouling ability of the degradable polymers by field tests. Our aim is to develop non-toxic, effective and durable antifouling materials.



Scheme 1 Structure of P(MMA-*co*-PEOCA) copolymer

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EXPERIMENTAL

Materials and Sample Preparation

Acrylate terminated poly(ethylene oxide-*co*-ethylene carbonate) was prepared following a procedure described elsewhere^[18–20]. The number average molecular weight (M_n) of the macromonomer determined by ¹H-NMR was 5300, and the molecular weight distribution index (M_w/M_n) estimated by gel permeation chromatography (GPC) was 1.32. The molar fraction of EC units estimated by ¹H-NMR based on the integrals of EC and EO signals was *ca.* 20 mol%. P(MMA-*co*-PEOCA) copolymers were synthesized by free radical polymerization. A certain amount of MMA, PEOCA, 2,2-azobisisobutyronitrile and THF were added into a three-neck flask equipped with an agitator, a reflux condenser and a gas inlet/outlet. After nitrogen-purge for 30 min, polymerization was carried out at 70°C for 24 h. The product was precipitated into ethyl ether and washed thoroughly with methanol to remove the unreacted macromonomer. The copolymer is designed as P(MMA-*co*-PEOCA x), where x is the weight percentage of PEOCA determined by ¹H-NMR. Namely, the PEOCA contents in P(MMA-*co*-PEOCA7), P(MMA-*co*-PEOCA30), P(MMA-*co*-PEOCA45) and P(MMA-*co*-PEOCA63) are 6.9 wt%, 30.4 wt%, 44.5 wt% and 63.2 wt%, respectively. The molecular weight values of the resultant copolymers are in the range 8.0×10^4 to 11.0×10^4 .

QCM-D Measurements

QCM-D measurements were performed on E1 system with 5 MHz AT-cut gold-coated quartz crystal (Q-Sense AB). The details can be found elsewhere^[21–24]. Briefly, QCM-D simultaneously monitors changes in resonance frequency (Δf) and dissipation (ΔD) in real time. Δf is related to the changes in the mass attached to the oscillating sensor surface, whereas ΔD is related to the viscoelasticity of the adsorbed layer. The evaluation of degradation was performed for *ca.* 48 h by exposing the P(MMA-*co*-PEOCA) film to natural seawater which was obtained from the site at the inner Xiamen Bay (24°45'N, 118°07'E) in China and filtered before use. The increase in the oscillation frequency corresponds to the loss of the film mass on the QCM sensor surface. All the presented data were from the third overtone ($n = 3$). Δf and ΔD values from the fundamental were discarded because they were usually noise due to insufficient energy trapping^[25]. All the experiments were performed at 25°C.

Field Tests in Seawater

The field tests were performed from May to November, 2011 at the inner Xiamen Bay (24°45'N, 118°07'E) in China, where the marine biofouling is heavy because of the rich fouling organisms. The panel (300 mm $\times$ 250 mm $\times$ 3 mm) used consisted of epoxy resin reinforced by glass fiber, and it was roughened before it was coated with P(MMA-*co*-PEOCA). The coated panels were dried completely at room temperature and were lowered into seawater at a depth of 0.2–2.0 m. After a certain period of time, the panels were taken out of the sea and carefully washed with seawater and photographed, and then they were immediately placed in the sea to continue the test. A set of panels coated with P(MMA-*co*-PEOCA63) was tested in contrast with control panels without any coating. For comparison, a set of panels coated with polyurethane with poly(ethylene glycol) (PEG) as the soft segment (PEG-PU50) was also examined, where the content of the soft segments is 50 wt%. As we reported before, PEG-PU50 demonstrates good protein resistance^[26].

RESULTS AND DISCUSSION

It is reported PEOC with carbonate linkage susceptible to hydrolysis can degrade in ethanol in the presence of potassium hydroxide^[18]. However, we do not know whether it is degradable or not in the natural, highly turbulent marine environment. Accordingly, we first examined the hydrolytic degradation of P(MMA-*co*-PEOCA) copolymers. Figure 1 shows the time dependence of frequency shift (Δf) and energy dissipation shift (ΔD) for the hydrolytic degradation of the P(MMA-*co*-PEOCA) with different PEOCA contents in natural seawater. As we know, Δf is related to the mass or thickness of the added layer on the sensor surface, whereas ΔD is to its thickness and viscoelasticity^[21, 24]. The changes in the frequency (Δf) and dissipation (ΔD) give the

information about the degradation of P(MMA-*co*-PEOCA) copolymers. For P(MMA-*co*-PEOCA30), P(MMA-*co*-PEOCA45) and P(MMA-*co*-PEOCA63), the sharp increase in Δf and decrease in ΔD demonstrates the mass loss of the P(MMA-*co*-PEOCA) film. Namely, some PEOC chains degrade into small molecules which disperse into the solution. Clearly, the degradation rate increases with PEOCA content, that is, P(MMA-*co*-PEOCA63) degrades most quickly. For P(MMA-*co*-PEOCA7), the slight Δf shift indicates the hydrolytic degradation is slow. On the other hand, ΔD increases with time, quite different from that for P(MMA-*co*-PEOCA) with higher PEOCA content. It is known that the hydrophilic PEOC side chains favor to be distributed on the surface of P(MMA-*co*-PEOCA) film when it is immersed in the seawater. PEOC side chains can cover the surface at a higher content so that their degradation leads the morphology and the thickness of the film to vary evenly. When PEOCA content is less than 7 wt%, PEOC side chains can not cover the surface completely. Namely, some PMMA segments are also exposed to the seawater. Thus, the degradation of PEOC side chains makes the surface rough and uneven, leading ΔD to increase.

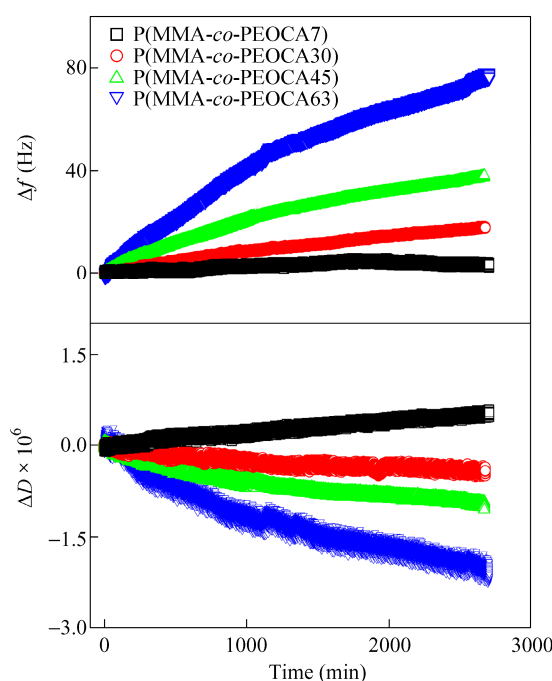


Fig. 1 Time dependence of frequency shift (Δf) and dissipation shift (ΔD) for hydrolytic degradation of P(MMA-*co*-PEOCA) with different PEOCA contents in natural seawater at 25°C

Figure 2 shows the ΔD versus Δf relation for different P(MMA-*co*-PEOCA) copolymers. The relation can reflect the kinetics of the degradation. When PEOCA content is above 30 wt%, the degradation involves only one stage, that is, ΔD linearly decreases with Δf . The fact indicates the thickness of the film linearly decreases or the film linearly degrades^[27]. For P(MMA-*co*-PEOCA7), ΔD increases with Δf . As discussed above, this is because the roughness of the film surface increases with the ongoing degradation. Anyhow, Fig. 1 and Fig. 2 indicate the P(MMA-*co*-PEOCA) copolymers are degradable and the degradation depends on the PEOCA content.

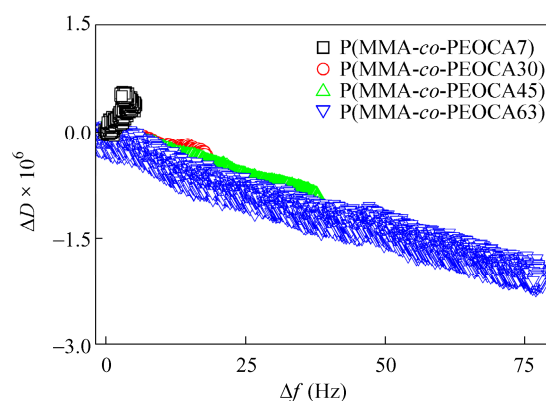


Fig. 2 ΔD versus Δf relation for hydrolytic degradation of P(MMA-*co*-PEOCA) with different PEOCA contents in natural seawater at 25°C

The anti-biofouling of the polymers was examined by marine field tests. Figure 3(a) shows the marine biofouling of control panels whose surfaces constructed by epoxy resin. During the time period from May until November 2011 at Xiamen, the coated panels had experienced heavy barnacle fouling due to the warm water environment and the stable salinity. The tested coatings can be screened quickly because coating failures can be observed within 4 weeks from immersion due to presence of juvenile barnacles on the surface. As expected, juvenile barnacles already grew on the surface in 4 weeks, and the test panels were fully encrusted by 12 weeks of exposure in marine environments. Figure 3(b) show the biofouling on the panels coated with P(MMA-*co*-PEOCA63) whose side chains are degradable. Clearly, the panels coated with P(MMA-*co*-PEOCA63) remain

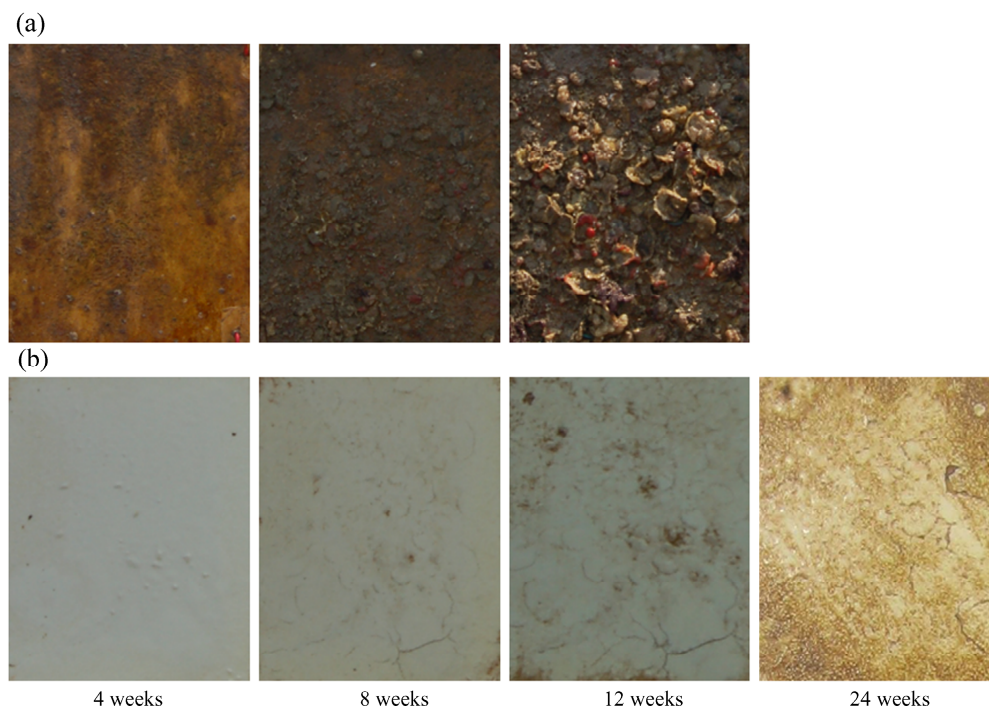


Fig. 3 Typical images of control panel without coating (a) and panels coated with P(MMA-*co*-PEOCA63) (b) after immersion in seawater at a depth of 0.6–1.0 m as a function of time

clean within 8 weeks and the surfaces still have good anti-biofouling after 12 weeks. Actually, the surfaces can effectively resist marine fouling except some sea slime within 24 weeks. Note that the P(MMA-*co*-PEOCA63) surface is different from that of the control panel in color because the latter is coated with epoxy resin.

The above studies demonstrate the copolymers with degradable PEOC side chains can effectively inhibit marine biofouling. As we know, PEOC side chains not only contain the degradable carbonates but also have ethylene oxide (EO) units with protein resistance^[28–32]. To understand the roles of degradation and protein resistance in anti-biofouling, we have also examined the surface constructed by PEG-PU50 which exhibits zero adsorption of proteins^[28], where the EO content (*ca.* 50 wt%) is close to that in P(MMA-*co*-PEOCA63). The field tests demonstrate that the surface is clean in 4 weeks. However, marine organisms already located on the surfaces within 8 weeks, and they were heavily fouled after 12 weeks. Accordingly, EO units can resist the fouling in a relatively short time. For a long term anti-biofouling, hydrolytic degradation is essential.

Actually, the biofouling in marine environments is very complex. Either organisms (bacteria, spores, diatoms and barnacles) or inorganics such as sea slime can lead to biofouling. Although a surface with only protein resistance does not accept the former, it allows the latter to accumulate on it and form a thin film for biological species to accommodate after a period of time. Accordingly, such a surface does not hold long-term anti-biofouling ability. Since PEOC side chains in P(MMA-*co*-PEOCA) copolymer are not only protein resistant but degradable, the polymer is expected to form a self-renewed surface with protein resistance, and the attached living organisms or inorganics can be detached in the degradation process. It implies that degradation of polymers could be a promising strategy for marine anti-biofouling.

CONCLUSIONS

We have prepared poly(ethylene oxide-*co*-ethylene carbonate) copolymers which can degrade in natural seawater. Field tests indicate that the polymer have good anti-biofouling ability in marine environment. The present study clearly demonstrates that hydrolytic degradation besides protein resistance should be taken into account when we design marine anti-biofouling materials.

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