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Biodegradable poly(ester)-poly(methyl methacrylate) copolymer for marine anti-biofouling

Guoxiong Dai[1], Qingyi Xie[1], Shanshan Chen, Chunfeng Ma*, Guangzhao Zhang

Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, PR China

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ABSTRACT

Being biodegradable and eco-friendly, polyesters are promising in marine anti-biofouling. However, the slow degradation and poor adhesion limit their applications. In the present work, we have prepared poly(ester)-poly(methyl methacrylate) copolymer via radical ring-opening copolymerization of 2-methylene-1,3-dioxepane (MDO) and methyl methacrylate (MMA). The copolymer coating has good adhesion to substrate due to the incorporation of MMA moieties. The main-chain ester bonds from MDO enable the copolymer to enzymatically and hydrolytically degrade, and the degradation rate increases with the ester content. The polymers can serve as a carrier and controlled release matrix for organic antifoulant 4,5-dichloro-2-octylisothiazolone (DCOIT), and the release rate increases with the ester content. Marine field test shows the system of the copolymer and DCOIT has excellent antifouling performance for more than 3 months.

1. Introduction

It is well known that marine biofouling often has detrimental effects on marine industries and other marine activities [1–3]. Antifouling coatings containing various biocides had long been used to prevent and control marine biofouling, particularly the tin-based self-polishing coatings. However, they were banned in 2008 due to their high toxicity to marine ecology [4]. To construct environmentally friendly antifouling systems, much effort has been paid to tin-free acrylate based self-polishing coatings [5–7], silicone based fouling release coatings [8–10], self-generated hydrogels [11–13], and slippery liquid infused surfaces [14,15]. Biodegradable polymers are recently developed antifouling materials [16–19]. They can form a dynamic surface that continuously renews and thus reduces the colonization of marine organisms [20]. They can also serve as the carrier and controlled release matrix of antifoulants. The degradable main chains enable the self-renewal of coating surface even at static immersion, quite different from traditional SPCs whose erosion is determined by the washing of flowing water. Biodegradable polymers finally decompose into small molecules in marine environment and do not give rise to the so-called microplastic pollution. Thus, the system consisting of biodegradable polymer and organic antifoulant is eco-friendly.

Note that biodegradable aliphatic polyesters such as polycaprolactone (PCL) and polylactic acid (PLA) can not be directly used in marine antifouling because of their poor adhesion and slow degradation due to high crystallinity [21–23]. Chemical modification [14] or blending [24,25] which lowers their crystallinity can significantly improve their performance in marine anti-biofouling.

On the other hand, polyacrylates are widely applied in coatings and adhesives owing to their remarkable film formation performance and adhesion to various substrates. Yet they are not degradable in marine environment. Biodegradable polyacrylates are promising in marine anti-biofouling because they are expected to exhibit advantages from both polyacrylates and biodegradable polymers. Radical ring-opening polymerization (RROP) of cyclic ketene acetals (CKAs) and vinyl monomers yields poly(vinyl-co-ester)s [26–28]. Such copolymers have low crystallinity due to the branched structure and hence a higher degradation rate [29,30]. Thus, RROP provides a facile and efficient strategy to obtain biodegradable polyacrylates. Compared with other biodegradable polymers such as PCL-based polyurethane [17], biodegradable polyacrylates are easier to synthesize and have better film forming ability. In the present study, we have synthesized poly(ester)-poly(methyl methacrylate) copolymer by RROP of 2-methylene-1,3-dioxepane (MDO) and methyl methacrylate (MMA). We have studied its enzymatic and hydrolytic degradation as well as the release of organic antifoulant. We also have examined its anti-biofouling performance by marine field tests. Our aim is to develop an eco-friendly and effective marine anti-biofouling system.

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* Corresponding author.
E-mail address: msmcf@scut.edu.cn (C. Ma).
[1] These authors contributed equally to the work.

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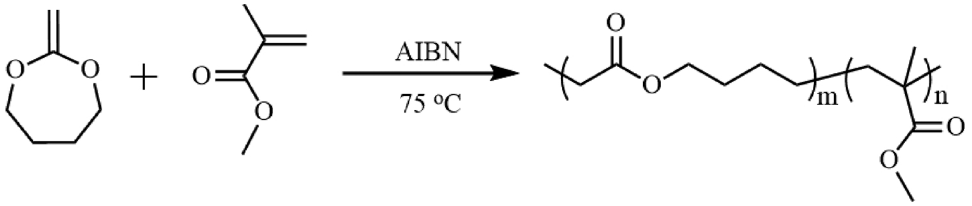

Scheme 1. The synthetic route of PMMx.

2. Experimental

2.1. Materials

2-Methylene-1,3-dioxepane (MDO) was synthesized following procedures detailed elsewhere [31]. Methyl methacrylate (MMA) from Aladdin was purified by distillation before use. 2,2-Azobisisobutyronitrile (AIBN) from Aladdin was recrystallized twice from methanol. 4,5-Dichloro-2-octylisothiazolone (DCOIT) was purchased from Baiao Chemical (Dalian, China) and used as received. 1,4-Dioxane was dried by CaH_2 and distilled before use. Artificial seawater (ASW) was prepared following ASTM D1141-98 (2013) [32]. Lipase was purchased from Sigma and used as received. Other reagents were used as received.

2.2. Synthesis of copolymer of MDO and MMA

As shown in Scheme 1 , the copolymer was synthesized by RROP in dioxane. Typically, 8.00 g of MMA (80.0 mmol), 2.28 g of MDO (20.0 mmol) and 0.82 g of AIBN (0.5 mmol) were dissolved in 10 mL of dioxane in a Schlenk tube and the reaction mixture was degassed by three freeze-evacuate-thaw cycles. The polymerization was performed under nitrogen at 75 °C for 24 h. The resultant polymer was precipitated in methanol and dried under vacuum at 70 °C overnight. ^{1}H-NMR (600 MHz, $CDCl_3$, ppm): 4.01 ($-CH_2COOCH_2CH_2CH_2CH_2-$), 3.63 ($-COOCH_3$), 2.48 ($-CH_2COOCH_2CH_2CH_2CH_2-$), 1.2–1.7 ($-CH_2COOCH_2CH_2CH_2CH_2-$). The copolymer is designated as PMMx, where x is the molar percentage of polyester determined by ^{1}H-NMR (Table 1).

3. Characterization

3.1. Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

^{1}H-NMR spectra were recorded on a Bruker AV600 NMR spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard.

3.2. Gel permeation chromatography (GPC)

The number-average molecular weight (M_n) and the polydispersity ($Đ_M$) were determined by Agilent gel permeation chromatography (1260 Infinity) with refractive index (RI) and ultraviolet (UV) detectors. The experiment was conducted in tetrahydrofuran (THF) at 35 °C using two identical PLgel columns (5 μm, MIXED-C) at a flow rate of 1.0 mL/min. Calibration was done with a series of narrowly dispersed polystyrene standards (1.30×10^3 to 2.21×10^6 g/mol).

Table 1
Characterization data of PMMx.

Sample	Feed molar ratio MDO/MMA	Molar composition [a] Polyester/MMA	M_n (kDa) [b]	$Đ_M$ [b]	T_g (°C) [c]
PMM0	0/100	0/100	22	2.6	113
PMM10	20/80	10/90	27	2.0	56
PMM31	50/50	31/69	26	2.0	17
PMM49	65/35	49/51	19	2.3	6

[a] Determined by ^{1}H-NMR.
[b] Determined by GPC.
[c] Determined by DSC.

3.3. Differential scanning calorimeter (DSC)

DSC test was performed on a NETZSCH DSC 204F1 differential scanning calorimeter under a nitrogen flow of 50 mL/min. The sample was quickly heated to 150 °C and equilibrated for 5 min to eliminate thermal history, and then it was cooled to −60 °C at a rate of 10 °C/min. Subsequently, it was heated to 150 °C at a rate of 10 °C/min. The glass transition temperature (T_g) was obtained from the endothermic shift during the second heating scan.

3.4. Adhesion test

The adhesion of PMMx coating on a glass fiber reinforced epoxy panel was measured using a pull-off adhesion tester (PosiTest AT-A Automatic). PMMx coating with a dry thickness of ~300 μm was prepared via solution casting where the polymer concentration in xylene was 30% (w/v). Pull-test adhesion data were obtained by detaching an aluminum dolly (20 mm in diameter) at a speed of 0.2 MPa/s at 25 °C. Five different points on each sample were tested to obtain an average value.

3.5. Hydrolytic degradation

The PMMx coating on an epoxy resin panel ($20 \times 20\ mm^2$) was prepared via solution-casting. Generally, solution of polymer in xylene (30%, w/v) was dripped onto the panel and dried in a fume hood at room temperature for 3 days and then under vacuum at 40 °C for 2 days to remove the solvent. The test was conducted in ASW at 25 °C. The initial weight (W_0) of each dried coating together with its panel was measured before the coating was immersed in ASW which was replaced every 2 weeks. At certain intervals, the sample was taken out and rinsed with deionized water. The sample was dried at 25 °C for 1 day and then freeze-dried for 3 days before their weights (W_t) were recorded. The mass loss was calculated by (W_0-W_t)/test area. For each polymer, three coated panels were prepared and measured to obtain an average value.

The molar mass of degradation product of PMMx was also studied under an accelerated condition. The solution of 100 mg of PMMx in 1 mL of THF was added into 6 mL of 0.1 M KOH methanol and stirred at 25 °C. At certain intervals, 1 mL of the mixed solution was taken out and neutralized with HCl. Afterwards, solvents were evaporated and the residue (polymer and KCl) was dissolved in chloroform and water. The chloroform solution was taken and solvent evaporation was done to obtain the degraded product of PMMx, which is analyzed with GPC.

3.6. Enzymatic degradation

The enzymatic degradation was measured by QCM-D from Q-sense AB (Sweden). PMMx film was prepared by spin-casting from polymer solution in THF (5.0 mg/mL) on AT-cut quartz crystal surface, and then dried at 60 °C for 24 h. The quartz crystal was placed in a fluid cell with the side of polymer film exposed to the solution. The lipase solution (1.0 mg/mL) was delivered to the surface at a flow rate of 150 μL/min using ASW as reference. Details of the QCM-D measurements can be found elsewhere [33]. Briefly, the shift in frequency (Δ*f*) of the crystal is