



Biodegradable polymer as controlled release system of organic antifoulant to prevent marine biofouling



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ABSTRACT

Controlled release of antifoulant is critical for marine antibiofouling. We have prepared polyurethane with degradable polyester segments consisting of poly(ethylene adipate) (PEA), poly(1,4-butylene adipate) (PBA) or poly(1,6-hexamethylene adipate) (PHA) and used it as the release system for organic antifoulants. The degradation rate of the polyurethane increases with the content of the degradable segments. On the other hand, as the segments change from PEA, PBA to PHA, the degradation rate decreases because the crystallinity increases but the ester group density decreases. Such degradable polyurethane allows the antifoulants to release at a constant rate, where the release rate can be regulated by varying the polyester segments. Marine field tests reveal that the polyurethane-antifoulant system has good antifouling performance. Particularly, the degradable polyurethane exhibits excellent adhesion to the substrate ensuring the long duration of the system.

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1. Introduction

Marine biofouling is a global problem for marine industry and marine activities. Heavy metal-containing self-polishing copolymers (SPCs) coatings are effective to combat marine fouling. However, they were banned because they are ecologically harmful with release of high-toxic biocides and non-degradable main chains [1–4]. Degradable polymers can form a self-polishing surface and serve as carrier and release system of antifoulants. Particularly, with the degradable main chains, they exhibit good antifouling performance on both dynamic and static conditions, quite different from the traditional SPCs which have very limited antifouling ability in static marine environment [5–11].

Recently, polyesters with degradable backbone have been used for marine antibiofouling. However, the high crystallinity usually leads to poor adhesion to substrates and slow down the degradation, which limits their application [6,7,12]. It is necessary to decrease the crystallinity and spherulite size to improve the adhesion and regulate the degradation [5,8,13]. In the present study, we have prepared degradable polyurethanes with poly(ethylene adipate) (PEA), poly(1,4-butylene adipate) (PBA) or poly(1,6-hexamethylene adipate) (PHA) segments whose monomers are

made from renewable resources [14–18]. The polyurethane was used as the carrier of organic antifoulant (4,5-dichloro-2-octylisothiazolone). We have investigated the degradation of the polyurethanes, the release of antifoulants and the antifouling and mechanical properties of the systems. Our aim is to develop an eco-friendly marine antifouling system with good antifouling performance and high adhesion to the substrate.

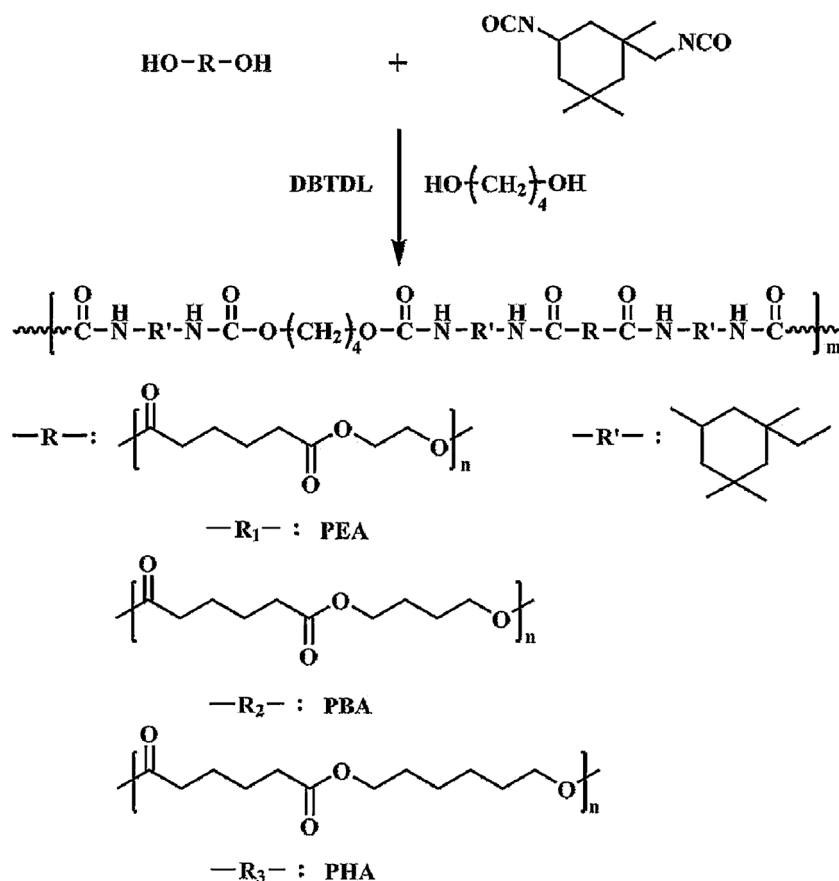
2. Experimental

2.1. Materials

Poly(ethylene adipate) diol (PEA, $M_w = 2000$ g/mol), poly(1,4-butylene adipate) diol (PBA, $M_w = 2000$ g/mol) and poly(1,6-hexamethylene adipate) diol (PHA, $M_w = 2000$ g/mol) from Xuchuan Chem were dried under reduced pressure for 2 h prior to use. 1,4-Butanediol (1,4-BD) from Aldrich was also dried in the same way. 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) from Aladdin and dibutyltin dilaurate (DBTDL) from Aldrich were used as received. Tetrahydrofuran (THF) was refluxed over CaH_2 and distilled prior to use. 4,5-Dichloro-2-octyl-isothiazolone (DCOIT) was kindly presented by Thankful Chemical Co. (Guangzhou). Artificial seawater (ASW) was prepared according to ASTM D1141-98 (2013) [19]. Other reagents were used as received.

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Scheme 1. Synthesis of polyester based polyurethane.

Table 1
 Characterization data of polyester based polyurethane.

Sample	x content (wt%) ^a	$M_n \times 10^{-4}$ (g/mol) ^b	\bar{M}_w ^b	T_g (°C)	T_m (°C)	ΔH_m (J/g)	$T_{50\%}$ (°C) ^d
PEA40-PU	39.3	13.7	1.32	-37.5	-	-	323
PEA60-PU	59.2	15.6	1.47	-33.1	-	-	341
PEA80-PU	79.1	14.4	1.42	-31.2	41.3	32.3	359
PBA80-PU	78.7	13.7	1.38	-44.6	44.6	36.3	357
PHA80-PU	78.6	13.5	1.39	-	49.8	45.1	348

^a Determined by ¹H NMR.

^b Determined by GPC.

^c Determined by DSC.

^d Temperature at 50% weight loss determined by TGA.

2.2. Synthesis of polyester-based polyurethane

Polyester-based polyurethane was synthesized by polyaddition (Scheme 1). First, IPDI reacted with polyester diol at 70 °C for 1 h in THF under 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 (Fig. S1, 600 MHz, CDCl₃, ppm): 4.07 (OCH₂CH₂CH₂CH₂O), 3.79 (CONHCH(CH₂)₂), 3.21, 2.91 (C(CH₃)CH₂NHCO), 2.35 (COCH₂CH₂CH₂CO), FTIR (Fig. S2, cm⁻¹): 3530 (OH), 3380 (NH), 2950 (CH₂), 1735 (C=O), 1530 (CN). For convenience, the polyester-based polyurethanes are designated as PEA_x-PU, PBA_x-PU, PHA_x-PU, where *x* represents the weight percentage of the polyester soft segment determined by ¹H NMR. The characterization data are summarized in Table 1 and the details can be found in the Supporting information (SI).

2.3. Polyester-based polyurethane characterization

¹H NMR spectra were recorded on a Bruker AV600 NMR spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard.

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 KBr disk method.

The number-average molecular weights (M_n) and molecular weight dispersity (\bar{M}_w) were determined by GPC at 50 °C on a Waters 1515. A series of monodisperse polystyrene were used as standard in the fluent of DMF and LiBr with a flow rate of 1.0 ml/min.

TGA measurement was performed on a NETZSCH TG 209F1 instrument under nitrogen atmosphere at a heating rate of 10 °C/min in the range from 30 to 800 °C. The decomposition temperature ($T_{50\%}$) of PEA-PU increases with the content of PEA segments. PEA80-PU has the best thermal stability (Table 1 and Fig. S3 in SI).

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