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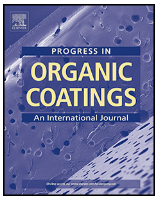

Antifouling activity of novel polyisoprene-based coatings made from photocurable natural rubber derived oligomers

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ABSTRACT

Natural rubber is a renewable resource with a potential as precursor of a very wide range of novel polymers, including polyisoprene-based surfaces with antifouling (AF) activity. In this work, new ionic and non-ionic coatings were prepared by the photocrosslinking reaction of photosensitive *cis*-1,4-oligoisoprenes, bearing a variable number of ammonium groups. The photochemical crosslinking was achieved using radical (via acrylate groups) or cationic (via epoxy groups) processes. Surface properties of these coatings were studied by static contact angle measurements and AFM imaging. Assessment of bioactivity demonstrated that most of the resulting coatings showed AF potential against fouling organisms: growth inhibition of marine bacteria (*Pseudoalteromonas elyakovii*, *Shewanella putrefaciens*, *Cobetia marina*, *Polaribacter irgensii*, *Vibrio aestuarianus*) and fungi (*Halosphaeriopsis mediosetigera*, *Asteromyces cruciatus*, *Lulworthia uniseptata*, *Zalerion* sp., *Monodictys pelagica*); decreased adhesion of microalgae (*Navicula jeffreyi*, *Cylindrotheca closterium*, *Chlorarachnion globosum*, *Pleurochrysis roscoffensis*, *Exanthemachrysis gayraliae*, *Amphora coffeaeformis*); inhibition of attachment and/or germination of spores of *Ulva intestinalis*. The best AF activity was obtained with the ionic surfaces. These new coatings prepared from precursors obtained from natural rubber are in essence active by contact. As the biocidal functions are fixed covalently to the polymer chain, detectable release of biocidal products in the marine ecosystem is prevented so that a valuable environment-friendly alternative for new AF coatings is hereby proposed.

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1. Introduction

The fouling phenomenon can be defined as the accumulation of micro- and macro-organisms on surfaces subsequent to immersion in an aquatic environment. More specifically, materials immersed in seawater are rapidly coated by a macromolecular film, which then favours colonization by prokaryotes (mostly bacteria), unicellular (microalgae) and multicellular eukaryotes, such as macroalgae, barnacles and mussels [1]. Biofouling represents a major nuisance for the maritime industry, especially for shipping, as biofouling on ship hulls increases the boat weight subsequently inducing over-consumption of fuel and increased maintenance costs [2–5]. Biofouling is also of great concern for offshore structures and aquaculture equipment [3,6–8]. This phenomenon is estimated to cause directly and/or indirectly losses to a country having a marine industry, as high as 7% of the gross national product [9]. To fight against biofouling, various copper and tributyltin (TBT) based coatings have been widely used. Tributyltin self-polishing copolymer paints (TBT-SPC paints) have been the most successful solution in combating biofouling on ships [2,10]. Unfortunately, these formulations have seriously affected marine ecosystems [11]. As a consequence, TBT use on small boats (less than 25 m in length) has been prohibited in many countries since the mid-1980s. An International Convention held on 5 October 2001 banned the application of TBT-based antifouling (AF) paints since 1/1/2003 and imposed a complete prohibition of the presence of such paints on ship hulls since the 1/1/2008.

The paint industry has been urged to develop TBT-free products and some less toxic materials have already been used, such as low molecular weight molecules (organic biocides, e.g., Irgarol 1051, Zinc pyrithione, Diuron, Sea-Nine 211^{TM}, Zineb) incorporated in a matrix [4,12–15]. The phenomena of slow release of these products in the environment and their toxicity have not been sufficiently well studied yet. However, several works have highlighted that

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these compounds are also harmful to the environment [13,14,16]. Non-stick, fouling-release (FR) coatings based on fluoropolymer and silicon were also developed [2,15]: they do not prevent settlement of fouling organisms, but reduce the attachment strength such that when the vessel is in motion, deposited organisms can be easily removed. FR coatings can exhibit poor adhesion to the substrate, are easily damaged (cutting, tearing and puncturing) and have poor mechanical properties [2], but research is conducted to overcome these drawbacks. Other non-toxic strategies include incorporating natural antifouling compounds from marine organisms into coatings [17–19], but no commercial formulation has been developed yet.

A promising alternative is to covalently bind biocidal functions on a polymer chain to avoid the release of biocide products and to maintain a permanent AF activity. A number of biocidal agents, such as quaternary ammonium (QA) salts, phosphonium salts, sulfonium salts, chlorophenyl derivatives and N-halamine have been introduced into ordinary polymers. In AF paints, QA salts are essentially found in polymers like polyurethanes [20–23], polysiloxane [15,24–26] and polymethacrylates [27,28]. It has been shown that ionic polyurethane containing oligoisoprene bearing ammonium groups have antibacterial activities [23] and such an alternative has been further investigated by fixing QA functions to a polymer stemming from renewable resources (natural rubber). Selective degradation of *cis*-1,4-polyisoprene using well-controlled oxidative chain cleavage leads to new carbonyl-telechelic polyisoprenes (CTPI) [29–31]. Chemical modifications of carbonyl end-groups and carbon–carbon double bonds led to new photosensitive oligomers (with or without QA groups). These oligomers have been crosslinked by radical way (via acrylate groups) and/or by cationic way (via epoxy groups) [30–32].

In the present work, we report the use of the previously described oligomers [30–32] in the preparation of new ionic and non-ionic coatings. After evaluation of their surface properties, the AF potency of these coatings was tested against the adhesion and growth of five strains of marine bacteria, five strains of marine fungi, six strains of marine microalgae and one strain of marine macroalgae involved in marine biofilm formation [33–35].

2. Materials and methods

2.1. Materials and instrumentation

Cis-1,4-polyisoprene (Acros Organics, 98% *cis*, $M_w = 800{,}000$) was used for the synthesis of cationomers and photosensitive oligoisoprenes. 2,2-Dimethyl-2-hydroxyacetophenone (Darocur 1173, Aldrich, Scheme 1) and hexafluoro-phosphate triarylsulfonium salt (Degacur KI85, Aldrich, Scheme 1) were used as photoinitiators. 3-Ethyl-3-hydroxymethyl oxetane (trimethylolpropane oxetane, TMPO, Aldrich, 90%, Scheme 1) has been used as reactive diluent for cationic radiation curing.

The ^{1}H NMR spectra were recorded on a Bruker 400 Fourier Transform spectrometer at 400.13 MHz, in $CDCl_3$ solutions using tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Fourier transform Perkin-Elmer 2000 spectrometer in ATR (attenuated total reflexion) mode. The number averaged molecular weight ($\overline{Mn}$) was measured at 35 °C on a ThermoFinnigan SEC instrument (equipped with a pre-column Polymer Laboratories (PL gel 5 μm Guard, 50 mm × 7.5 mm) and two columns Polymer Laboratories (2PL gel 5 μm MIXED-D columns, 2 mm × 300 mm × 7.5 mm)). The calibration was performed using polystyrene standards ($580–483 \times 10^3$ g/mol) and the molecular weights corrected by the Benoît factor [36].

2.2. Syntheses

2.2.1. Synthesis of cationomers and photosensitive oligoisoprenes

Cationomers (acrylate PI, epoxidized PI and diacrylate PI, Scheme 1), epoxidized hydroxytelechelic *cis*-1,4-polyisoprene (EHTPI) and diacrylate *cis*-1,4-polyisoprene (diacrylate PI) (Scheme 1) were synthesized from carbonyltelechelic *cis*-1,4-polyisoprene (CTPI) according to a methodology previously described [30–32]. Scheme 2 summarizes the synthetic route.

Carbonyltelechelic *cis*-1,4-polyisoprene (CTPI, see Scheme 2) was obtained by controlled degradation of high molecular weight *cis*-1,4-polyisoprene. For the present work, in order to obtain 2000 g/mol molecular weight oligomers, m-chloroperbenzoic acid (*m*-CPBA) (3.62 g) (Aldrich, 70%) in 100 mL of dichloromethane were added dropwise to a solution of *cis*-1,4-polyisoprene (20 g) in 500 mL of dichloromethane into a jacketed flask cooled at 0 °C (reaction time: 6 h). To the purified epoxidized *cis*-1,4-polyisoprene (epoxide ratio = 5%, 18 g) dissolved in 400 mL of tetrahydrofuran (THF), periodic acid (3.43 g) (Acros, 99%), in 50 mL of THF was added dropwise in a jacketed reaction flask at 30 °C (reaction time: 6 h) (yield = 90–95%).

^{1}H NMR of CTPI ($CDCl_3$) δ (ppm): 5.10 (t, $=CH_{isoprenic}$), 2.05 (m, $CH_{2\ isoprenic}$), 1.67 (s, $CH_{3\ isoprenic}$), 9.77 (s, $CH_2C\underline{H}O$), 2.49 (m, $C\underline{H_2}CHO$), 2.34 (m, $C\underline{H_2}CH_2CHO$), 2.13 (s, $C\underline{H_3}CO\ CH_2$), 2.43 (s, $CH_3COC\underline{H_2}CH_2$), 2.25 (m, $CH_3COCH_2C\underline{H_2}$).

FTIR: $\nu_{C=C} = 1664\ cm^{-1}$; $\nu_{=CH} = 3035\ cm^{-1}$; $\nu_{C=O} = 1721\ cm^{-1}$; $\delta_{=C-H} = 834\ cm^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm^{-1}.

$\overline{Mn}$ (SEC) = 2600 g/mol; $\overline{Mn}$ (after correction by the Benoît factor) = 1742 g/mol; $\overline{Mn}$ (NMR) = 1732 g/mol.

Hydroxytelechelic *cis*-1,4-polyisoprene (HTPI, see Scheme 2) was prepared by a selective reduction of CTPI using $NaBH_4$. Typically, CTPI was dissolved in THF ([CTPI] = 0.07 mol/L) and it was added dropwise to a solution of sodium borohydride ($NaBH_4$, Acros, 98%) (4 equiv.) dissolved in 30 mL of THF. After stirring for 6 h at 60 °C, the mixture was hydrolyzed with ice, washed using saturated solution of NaCl and dried over $MgSO_4$ (yield = 93–98%).

^{1}H NMR of HTPI ($CDCl_3$) δ (ppm): 5.10 (t, $=CH_{isoprenic}$), 2.05 (m, $CH_{2\ isoprenic}$), 1.70 (s, $CH_{3\ isoprenic}$), 3.80 (m, $C\underline{H}OH$), 3.65 (t, $C\underline{H_2}OH$), 1.20 (d, $C\underline{H_3}CHOH$).

FTIR: $\nu_{C=C} = 1664\ cm^{-1}$; $\nu_{=CH} = 3035\ cm^{-1}$; $\nu_{OH} = 3350\ cm^{-1}$; $\delta_{=C-H} = 834\ cm^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene =1448, 1376 cm^{-1}.

$\overline{Mn}$ (SEC) = 2700 g/mol; $\overline{Mn}$ (after correction by the Benoît factor) = 1800 g/mol; $\overline{Mn}$ (NMR) = 1736 g/mol.

From HTPI, epoxidized hydroxytelechelic *cis*-1,4-polyisoprene (EHTPI) and diacrylate *cis*-1,4-polyisoprene (diacrylate PI) were obtained by epoxidation using mCPBA (in dichloromethane) and esterification with acryloyl chloride (in dichloromethane and catalyzed by triethylamine) respectively.

^{1}H NMR of EHTPI ($CDCl_3$) δ (ppm): 5.10 (t, $=CH_{isoprenic}$), 2.05 (m, $CH_{2\ isoprenic}$), 1.70 (s, $CH_{3\ isoprenic}$), 2.69 (t, $CH_{epoxide\ ring}$), 1,29 (s, $CH_{3\ epoxide\ ring}$), 3.80 (m, $C\underline{H}OH$), 3.65 (t, $C\underline{H_2}OH$), 1.20 (d, $C\underline{H_3}CHOH$).

^{1}H NMR of diacrylate PI ($CDCl_3$) δ (ppm): 5.10 (t, $=CH_{isoprenic}$), 2.05 (m, $CH_{2\ isoprenic}$), 1.70 (s, $=CH_{3\ isoprenic}$), 4.20 (t, $C\underline{H_2}O$), 5.01 (m, $C\underline{H}O$), 1.20 (d, $C\underline{H_3}CHO$), 6.15 (m, $C\underline{H}=CH_2$), 6.42 (t, $CH=C\underline{Ha}H$), 5.80 (q, $CH=CH\underline{Hb}$).

FTIR of EHTPI: $\nu_{C=C} = 1664\ cm^{-1}$; $\nu_{=CH} = 3035\ cm^{-1}$; $\nu_{OH} = 3350\ cm^{-1}$; $\delta_{=C-H} = 834\ cm^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm^{-1}; $\nu_{C-O(epoxide)} = 870\ cm^{-1}$.

FTIR of diacrylate PI: $\nu_{C=C(isoprene)} = 1664\ cm^{-1}$; $\nu_{=CH} = 3035\ cm^{-1}$; $\delta_{=C-H} = 834\ cm^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm^{-1}; $\nu_{C=O(ester)} = 1736\ cm^{-1}$; $\nu_{C=C(acrylate)} = 1632\ cm^{-1}$; $\delta_{=C-H_2\ (acrylate)} = 1408\ cm^{-1}$; disappearance of ν_{OH} at 3350 cm^{-1}).

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