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Fouling-release and chemical activity effects of a siloxane-based material on tunicates

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ABSTRACT

The antifouling performance of a siloxane-based elastomeric impression material (EIM) was compared to that of two silicone fouling-release coatings, Intersleek 757 and RTV-11. In field immersion trials, the EIM caused the greatest reduction in fouling by the solitary tunicate *Ciona intestinalis* and caused the longest delay in the progression of fouling by two species of colonial tunicate. However, in pseudobarnacle adhesion tests, the EIM had higher attachment strengths. Further laboratory analyses showed that the EIM leached alkylphenol ethoxylates (APEs) that were toxic to *C. intestinalis* larvae. The EIM thus showed the longest duration of chemical activity measured to date for a siloxane-based coating (4 months), supporting investigations of fouling-release coatings that release targeted biocides. However, due to potential widespread effects of APEs, the current EIM formulation should not be considered as an environmentally-safe antifoulant. Thus, the data also emphasize consideration of both immediate and long-term effects of potentially toxic constituents released from fouling-release coatings.

1. Introduction

Antifouling coatings can be divided into two broad categories: chemically-active coatings that release active compounds that kill or otherwise deter organisms from settling on a surface, and non-toxic fouling-release coatings that weaken adhesion of organisms and facilitate their release. To date, the most effective chemically active coatings have been based on heavy metals, many of which were banned due to their negative effects on the environment (reviewed by Yebra et al., 2004; Almeida et al., 2007). Consequently, numerous alternatives have been tested, including chemically-active coatings using enzymes or other natural products (eg Dobretsov et al., 2006, 2013; Fusetani, 2011; Qian et al., 2010), as well as a range of fouling-release coatings (reviewed by Almeida et al., 2007; Lejars et al., 2012). The most effective fouling-release coatings have been those based on polydimethyl siloxane (PDMS). The low surface energy and elastic modulus of PDMS elastomers decreases the strength of attachment of marine organisms. A large number of these siloxane-based fouling-release coatings have been tested (eg Holm et al., 2000; Swain et al., 2000; Terlizzi et al., 2000), together with additional studies of composition variants intended to enhance antifouling performance (eg Carl et al., 2012; reviewed by Lejars et al., 2012; Martinelli et al., 2012; Rahman et al., 2011).

Although siloxane-based coatings tend to have lower toxicity than chemically-active coatings that deliberately release biocides, there is still the possibility that these nominally fouling-release coatings leach chemicals that can either directly affect fouling organisms or have more downstream effects in the environment. A few of studies have considered this possibility (Nendza, 2007), and most have found acute toxic effects of leachates (Feng et al., 2012; Rittschof and Holm, 1997; Truby et al., 2000; Watermann et al., 1997). Thus it is important that tests of anti-fouling performance for siloxane-based coatings consider both physical and chemical mechanisms.

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The problematic fouling organisms that motivated this study are tunicates. Tunicates are prominent members of marine fouling communities that have caused considerable ecological and socio-economical impacts in some geographic locations (Reviewed by Aldred and Clare, 2014; Bullard et al., 2010; Lambert, 2001; Lambert and Lambert, 2003; Simkanin et al., 2013). Tunicate fouling has been particularly troublesome for some aquaculture operations worldwide, creating increased operation costs and decreased yield and product quality (Adams et al., 2011; Carman et al., 2010; Fitridge et al., 2012). Eradication techniques used in shellfish aquaculture have focused on chemical or physical treatments to remove tunicates after fouling has occurred (Arens et al., 2011; Carver et al., 2003; LeBlanc et al., 2007; Parent et al., 2011; Piola et al., 2010) Thus, the overall goal of this study was to test the performance of a silicone-based coating at limiting tunicate fouling.

The coating tested was chosen based on a serendipitous discovery of its antifouling properties. Vinyl siloxane polymers (VSP) are vinyl terminated PDMS elastomers that have outstanding impression accuracy, and are widely used as dental molds (Mandikos, 1998). VSPs have also been employed for biofouling studies, including testing their fouling-release characteristics (Kim et al., 2008), using them as matrices for dual-function biocidal and fouling-release coatings (Choi et al., 2007), and using them as molding materials for testing natural surface topographies that resist fouling (Scardino and de Nys, 2004). In a preliminary study, an elastomeric impression material (EIM, a commercial dental mold formulation of VSP) was used to create molds with different topographies that were then submerged at a site in Nova Scotia, Canada with a non-indigenous tunicate infestation. Although no effect of topography was found, little tunicate fouling accumulated on the EIM molds, and those organisms that did attach were easy to remove (Phillips, Bishop and Wyeth, 2013, unpublished observations). Based on this preliminary result, surface topography was eliminated from subsequent experimentation, and, instead, it was hypothesized that fouling-release characteristics exhibited by the EIM caused the reduced tunicate fouling. The first specific aim of this study was to test the fouling-release hypothesis, assessing the performance of the EIM relative to other silicone-based coatings in field immersion trials and pseudobarnacle adhesion tests. The second aim was to test the alternate possibility of chemical activity, using larval toxicity assays and chemical analyses to gather evidence regarding any leachates from the material.

2. Materials and methods

2.1. Coating treatments

The antifouling performance of an EIM was compared to that of uncoated polyvinyl chloride (PVC) controls and two commercially available coatings acting as performance references. Medical-grade EIM (Kerr Corporation, Part 29036) was prepared according to package instructions. The two reference treatments were Intersleek 757 (INT, International Coatings Ltd.), a silicone-based fouling-release coating system, and RTV-11 (RTV; Momentive Performance Materials Holdings LLC), a commercially available silicone known to have fouling-release properties (Holm et al., 2000, 2006; Kavanagh et al., 2003; Truby et al., 2000; Wynne et al., 2000). Both INT and RTV were prepared in accordance with manufacturer instructions and applied using paintbrushes. The INT coating was comprised of Parts BXA757, BXA758, and BXA759 and the back plates were first coated with Intershield 300 primer (Parts ENA301 and ENA303) and Intersleek 731 tiecoat formula (Parts BXA730 and BXA381). All coatings were applied to PVC back plates (25 cm × 15 cm), with controls left as bare PVC (see Table 1 for physical characteristics of the coatings). Nylon bolts were required to secure the EIM to the back plate, since no attachment system is available for this material. For consistency, nylon bolts were also placed on all other treatments. No mechanical damage was observed on any of the coatings during the study, with the exception of one RTV-coated plate that sustained partial detachment of a 6 cm^2 area that was still possible to include in the analysis.

Table 1
Thicknesses and contact angles of the coatings compared in field immersion trials. Mean and standard deviation ($n = 6$) for static contact angles were calculated for the silicone-based coatings and the bare PVC control plates. Since water drops changed shape considerably over the first 2 min of exposure to EIM (presumably due to surfactant leaching), drops were measured twice for this coating: immediately after placing the drop on the surface and again 3 min later. All other coatings showed unchanging contact angles.

Coating	Thickness (mm)	Contact angle (°)	
		Mean	St. Dev.
PVC Control	–	74.3	3.4
EIM (0 min)	3.0	68.8	6.9
(3 min)		39.9	1.1
RTV	0.5	104.7	1.8
INT	1.0	104.2	1.9

2.2. Field immersion trials

2.2.1. Sites

Field immersion tests were conducted at two sites in Nova Scotia, Canada where previous observations indicated invasive tunicates were prevalent: Strait of Canso Yacht Club (decimal degrees of latitude and longitude: 45.6134, -61.3653), in Port Hawkesbury, infested with *Ciona intestinalis*, and Cribbons Point Marina (45.7558, -61.8971), on the Northumberland Strait, where both *Botryllus schlosseri* and *Botrylloides violaceous* are abundant.

Sets of four test plates, one for each treatment, were attached with nylon cable-ties to rectangular frames constructed from standard household acrylonitrile butadiene styrene pipe. Ten replicate frames were submerged along a dock at each test site, with frames (separated by 0.5 m–3 m) suspended vertically 1 m below the water surface and oriented away from direct sunlight. Within frames, treatment plate order was varied systematically, such that each treatment was adjacent to the other treatments an equal number of times.

2.2.2. Fouling measurement

Fouling accumulation, as measured by cover area, was quantified based on a modification of ASTM D3623 (2012). A time-series of plate images was used, allowing non-destructive quantification of temporal changes of fouling. Plates were submerged on the 26 and 27 of June 2013, and temporarily raised out of the water and photographed 14 times (at weekly intervals over 12 weeks, and then after 14 and 17 weeks). The camera (Nikon Coolpix S5100) was mounted on a box fitted on the inside with a perimeter of LED lights to ensure similar lighting conditions among photographs. To reduce interference from organisms attached to the uncoated sides of the back plates, images were cropped to the 22.0 cm × 11.7 cm rectangular area inside the bolts (257 cm^2 total area, final resolution: 3400 × 1750 pixels). Seascape software (Teixidó et al., 2011) was used to segment downgraded images (850 × 437 pixels) into pixel regions based on color. Segmented regions were categorized manually as background (bare surface), *C. intestinalis*, colonial tunicates (*B. schlosseri* and *B. violaceous*), bryozoans (*Bugula* sp), colonial hydroids (species not identified), other fouling organisms, or unknown (when obscured by growth from outside the plate).