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Novel Approach to Anti-Fouling and Fouling-Release Marine Coatings Based on Dual-Functional Siloxanes

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Summary: The preparation, characterization, and bio-testing of biocide incorporated silicone coatings for marine applications have been conducted. Derivatives of the biocide, Triclosan (5-chloro-2-(2, 4-dichlorophenoxy) phenol), were used to covalently attach the biocide moiety to a silicone backbone. The formulation process allowed for control of the resulting coating's mechanical properties as well as antifouling/fouling-release performance in ocean site testing. The test results showed significantly reduce macro-fouling with sustained fouling-release characteristics for the coatings produced.

Keywords: biomaterials; coatings; elastomers; polymer; polysiloxanes; silicones

Introduction

Biological fouling of surfaces exposed to an aquatic environment such as ship hulls and offshore marine structures is a serious problem.[1] For example, biofouling on ship hulls reduces ship speed, maneuverability, and range, which impede mission performance.[2] In addition, fouling increases fuel consumption by as much as 30–40% and necessitates extensive maintenance, which raises the overall costs of operation.[3] Biocidal coatings contain metal or organic compounds (e.g., organotin or copper compounds) toxic to fouling entities and hence, deter settlement on the hull surface. Unfortunately, in spite of the effectiveness of these coatings at reducing hull fouling, the application of biocidal coating materials has been significantly reduced by the International Maritime Organization due to environmental concerns.

Non-toxic fouling-release coatings do not inherently protect against fouling settlement, but as the ship moves through the water the shear forces on the hull allow for some degree of fouling removal and self-cleaning.[4] The most common fouling-release coatings are based on highly fluorinated polymers[5] or polysiloxanes.[6] Although these coatings can provide fouling-release, their inadequate adhesion to the substrate, low durability, and high cost has limited their penetration into the marine coating market.[7]

Each of these two parallel lines of coatings research and development aimed at counteracting bio-fouling has produced elements of success but each continue to have serious problem areas which demand solutions. Interestingly, while each approach is aimed at solving the same problem, these two lines of R & D have had a minimum of overlap. As a result, we have focused our efforts on the development of novel, dual-functional marine coatings which are non- or less toxic than conventional marine coatings and possess aspects of both fouling-release and anti-fouling coatings.

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Materials

Triclosan (5-Chloro-2-(2,4-dichlorophenoxy) phenol) was purchased from Alfa Aesar (Ward Hill, MA). All vinyl-terminated

polydimethylsiloxanes (DMS-V42, VDT-731), methacrylpropyl-terminated polydimethylsiloxane (DMS-R3), silicone dioxide (SIS6962.0), brown pigment (PGBRN01), and Karstedt's catalyst (platinum (0) -1, 3-divinyl-1, 1,3,3-tetramethyl disiloxane complex) were purchased from Gelest (Morrisville, PA). A polyhydrosiloxane-based curing agent (T2-Cure) was purchased from Dow Chemical. MQV-6 was purchased from Clariant. Acryloyl chloride, methacryloyl chloride, and triethylamine were obtained from Aldrich Chemical (Milwaukee, WI). All chemicals were used as received.

Experimental Part

Synthesis and Formulation of Coating Materials

AcT (Acrylic acid, 5-chloro-2-(2, 4-dichlorophenoxy)phenyl ester):[8] Triethylamine (18.8 mL, 0.134 mol) was added dropwise to a solution of triclosan (30.0 g, 0.104 mol) and acryloyl chloride (10.9 mL, 0.134 mol) in THF (150 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature. After the solvent was evaporated under vacuum, 100 mL of both hexane and water were then added to dissolve the product and salt. The organic layer was extracted, washed once more with 100 mL of water, dried, and passed through a basic-Al_2O_3 column. The solvent of the clear eluent was evaporated at room temperature under vacuum, and the final product was obtained as a thick clean liquid in 88.7% yield. Crystallization at low temperature from a hexane solution provided colorless crystals with a melting point of 48.2 °C. ^{1}H NMR ($CDCl_3$): δ 5.99 (d, 1H), 6.23 (q, 1H), 6.49 (d, 1H), 6.84 (t, 2H), 7.17–7.25 (m, 3H), 7.43 (d, 1H). ^{13}C NMR ($CDCl_3$): δ 120.40, 120.52, 124.55, 126.04, 126.84, 127.16, 128.24, 129.35, 129.56, 130.45, 133.65, 141.68, 146.83, 151.14, 163.33.

MeT (Methacrylic acid, 2-methyl, 5-chloro-2-(2, 4-dichlorophenoxy)phenyl ester): The same procedure used for the synthesis of AcT was used to produce MeT with the exception that methacryloyl chloride replaced acryloyl chloride at an equivalent molar amount. The yield obtained was 67.1%. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 3H), 5.68 (s, 1H), 6.18 (s, 1H), 6.88 (d of d, 2H), 7.12–7.25 (m, 3H), 7.41 (d, 1H). ^{13}C NMR ($CDCl_3$): δ 18.31, 120.01, 120.78, 124.69, 125.77, 127.03, 128.14, 128.22, 129.31, 129.55, 130.41, 134.90, 142.14, 146.59, 151.34, 164.68.

vMeS (vinyl- and methacryloxypropyl-terminatined polydimethylsiloxane): 3.5 g. silicon dioxide was added to 40 g. vinyl terminated polydimethylsiloxane (DMS-V42) and mixed at high speed using a FlakTech speedmixer for one minute. Then, 20 g. methacryloxypropyl-terminated polydimethylsiloxane (DMS-R31), 0.2 g. trimethylsiloxy-terminated, vinylmethylsiloxane–dimethylsiloxane copolymer (VDT-731), and 1.44 g. brown pigment were added by syringe to the DMS-V42/silicon dioxide mixture and the blend mixed for one minute with the FlakTech speedmixer. 10 g. of MQV vinyl resins in xylene was added by pipette, premixed with a spatula and 14 drops of Karsedt's regent was added by pipette to the mixture and premixed by hand before mixing at low speed with the FlakTech speedmixer. A total of three batches were made this way and refrigerated for storage.

vMeS+6AcT (vinyl- and methacryloxypropyl-terminated polydimethylsiloxane with 6% acryltriclosan): 3.5 g. silicon dioxide was added to 40 g. vinyl-terminated polydimethylsiloxane (DMS-V42) and mixed at high speed using a FlakTech speedmixer for one minute. Then, 20 g. methacryloxypropyl-terminated polydimethylsiloxane (DMS-R31), 0.2 g. trimethylsiloxy-terminated, vinylmethylsiloxane–dimethylsiloxane copolymer (VDT-731), and 1.44 g. brown pigment were added by syringe and the whole mixture mixed using the FlakTech for a minute. Subsequently, 10 g. of MQV vinyl resins in xylene was added by pipette, premixed with spatula, and 0.3 mL of Karsedt's regent was added by syringe and premixed by hand before

mixing at low speed with the FlakTech speedmixer. A total of three containers were made this way and refrigerated for storage. 9 g. acrylated triclosan and xylene, 1:1 by weight, was added to each mixture before coating application.

vMeS+6MeT (vinyl- and methacryloxypropyl-terminated polydimethylsiloxane with 6% methacryltriclosan): 3.5g silicon dioxide was added to 40 g. vinyl-terminated polydimethylsiloxane (DMS-V42) and mixed at high speed using a FlakTech speedmixer for one minute. Then, 20 g. methacryloxypropyl-terminated polydimethylsiloxane (DMS-R31), 0.2 g. trimethylsiloxy-terminated, vinylmethylsiloxane–dimethylsiloxane copolymer (VDT-731), and 1.44 g. brown pigment were added by syringe and the whole mixture mixed for a minute with the FlakTech speedmixer. Subsequently, 10 g. of MQV vinyl resins in xylene was added by pipette, premixed with a spatula, and 0.3 mL of Karsedt's regent added by syringe to the mixture and premixed by hand before mixing at low speed with the Flaktech speedmixer. A total of three containers were made this way and refrigerated for storage. 9 g. methacrylated triclosan and xylene, 1:1 by weight, was added to each mixture before coating application.

vS (vinyl-terminated polydimethylsiloxane): 90 g. vinyl-terminated polydimethylsiloxane (DMS-V42), 90 g. vinyl-terminated polydimethylsiloxane (DMS-V31), 0.6 g. trimethylsiloxy-terminated, vinylmethylsiloxane–dimethylsiloxane copolymer (VDT-731), and 4.32 g. brown pigment were added by syringe to a polypropylene specimen cup. Then, 30 g. of MQV vinyl resins in xylene was added by pipette and the whole mixture was mixed mechanically using a stainless steel coiled stir rod attached to a Tallboys stirrer for approximately two minutes. Subsequently, 14 drops of Karsedt's regent was added by pipette to the mixture and the mixture allowed to mix for an additional ten minutes. 10.5 g. silicon dioxide was then added over approximately a 20 minute period using continuous mixing. The mixture was allowed to mix for an additional hour.

vS+6MeT (vinyl-terminated polydimethylsiloxane with 6% methacryltriclosan): 4.38 g. silicon dioxide was added to 37.5 g. vinyl-terminated polydimethylsiloxane (DMS-V42) and mixed at high speed using a FlakTech speedmixer for one minute. Then, 37.5 g. methacryloxypropyl-terminated polydimethylsiloxane (DMS-R31), 0.25 g. trimethylsiloxy- terminated, vinylmethylsiloxane–dimethylsiloxane copolymer (VDT-731), and 1.8 g. brown pigment were added by syringe and the whole mixture mixed with the FlakTech speedmixer for one minute. Subsequently, 12.5 g. of MQV vinyl resins in xylene was added by pipette along with 0.1ml of Karsedt's regent and premixed with spatula before mixing at low speed with the FlakTech speedmixer. A total of three batches were made this way and refrigerated for storage.

Panel Preparation and Field Testing

Coatings were applied on $4'' \times 8''$ marine grade aluminum panels. The panels were sand blasted and primed with International Marine coating primer, Intergard 264, using a draw down bar. Two commercially available coatings were utilized as controls to compare the antifouling and fouling-release properties of the experimental

Table 1.
A list of coatings used for this study. PDMS = polydimethylsiloxane.

Coatings	Description
vS+6MeT	Vinyl PDMS + 6% methacryltriclosan
vS	Vinyl PDMS
vMeS	Vinyl PDMS + methacryloxypropyl PDMS in 1:1 w/w ratio
vMeS+6AcT	vMeS + 6% acryltriclosan biocide
vMeS+6MeT	vMeS + 6% methacryltriclosan biocide

coatings in testing. The control coatings were Intersleek 425 (fouling-release coating from International Paints, U.K.) and Interspeed BRA 642 (copper ablative anti-fouling coating from International Paints, U.K.).

Static immersion tests were carried out by researchers at Florida Institute of Technology in the Indian River Lagoon (Melbourne, FL). All panels were held one meter below the water surface inside 1/2″ galvanized mesh cages. This was done to protect the panels from possible fouling interuption by unwanted aquatic species such as fish. Four replicates of each coating were used for the immersion studies and the fouling ratings of the coatings were determined based on ASTM D5618-94 fouling rating method. The static immersion studies of these coatings were carried out between April 2004 and July 2004. Two inspections were done on these coatings; one after 29 days and another after 85 days of immersion. Fouling rating (FR) is defined by FR = 100 – the sum of fouling % coverage (not including slime), i.e., FR 100 is a surface free of macro fouling.

Contact Angle and Tensile Modulus Measurement

Tensile modulus was measured on four replicates of dumbbell shaped Die C coating films under ASTM D412 method using Instron 5542 Instrument with Instron Bluehill 2.0 software. Procedure: Four duplicates punched using Die C dumbbell-shaped die. Die C has an overall length of 4.5 inches with a narrow section 1.31 inches long. This provides a gauge length 1 inch long and a gauge width of 0.25 inch. Carver press exerting approximately two metric tons of force was used. Specimens were measured in three separate places on stem and then averaged to give thickness measurement. Clamps applied to both ends above where the specimen begins to curve, while attempting to keep clamp pressure equal.

The water contact angle of the coatings were measured using a Symyx Technologies Incorporated Coating Surface Energy System. This automated system measures the contact angle of coatings by placing three droplets of liquid on the two standard 4x8 inch metal coating panels. The contact angle of each is measured using image analysis and the readings are averaged for both water.

Results and Discussions

The concept investigated involved combining characteristics of an antifouling coating with the characteristics of a fouling-release coating to produce novel, enviromentally-friendly marine coaitngs. The antifouling character of the coatings should deter settlement of marine organisms while the fouling-release character should allow easy release of organisms if the coating should become fouled at some point in its' lifetime. Since polysiloxanes are known to produce surfaces that allow for easy release of marine organisms, polysiloxanes were used as the coating matrix. To incorporate antifouling character into the coatings while maintaining low or no environmental toxicity, an organic biocide, namely, triclosan, was derivatized and chemically bound to the polysiloxane matrix. Thus, the coatings function using a dual function mechanism (antifouling and easy fouling release) in order to reduce the microfouling (bacterial biofilms, slime, Ulva, bryazoans, diatoms, etc.) and macrofouling (e.g. barnacles, muscles, tubeworms, etc.) on ship's hull with minimum environmental impact.

The biocide used in this study, Triclosan, is a broad spectrum antibacterial/antimicrobial agent used in various personal care and consumer products such as shampoo, toilet soap, deodorants, toothpaste, footwear and plastic ware. In this study, Triclosan was modified with (meth)acrylate moieties and incorporated into a silicone matrix through the well-known hydrosilation reaction. Figure 1 displays the a generic structure of the functionalized silicone matrices produced.

Both AcT and MeT were synthesized by esterfication of acryl chloride and

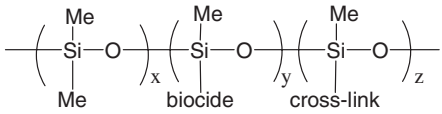

Figure 1.
General structure of silicone resins.

methacryl chloride, respectively, with Triclosan in the presence of an amine. Successful synthesis was confirmed using multi-nuclear NMR.

Two different base resins were chose for this study in order to change the mechanical properties of the coatings. The two base resins were a vinyl-terminated PDMS (DMS-V42) with molecular weight 72,000 g/mole and a methacryloxypropyl-terminated PDMS (DMS- R31) with a molecular weight 25,000 g/mole. The base resins were cured using a polyhydrosiloxane-based curing agent (T2-Cure). AcT or MeT was added to some coatings during their formulation to incorporate antifouling characteristics.

The physical and chemical characteristics of the coatings such as surface energy, tensile modulus, and glass transition temperature were measured in order to determine the correlation between chemical structure and antifouling/fouling-release performance. Surface energy has been previously shown to be an important factor for fouling-release performance.[9] However, using this measurement in isolation to assess fouling performance yields results which must be interpreted in context, because some organisms prefer to settle on hydrophobic surfaces, while others prefer hydrophilic surfaces.[10] In addition, some organisms can alter the phenotype of their secreted adhesive based on the surface energy of the substrate. The water contact angle value for all the coatings produced were between 106 and 116 degree as shown in Figure 2.

It has been demonstrated that bioadhesion to surfaces is directly proportional to the bulk modulus of elasticity.[11] Coatings possessing a low elastic modulus facilitate marine adhesive failure via a peel mechanism which allows the adhesive to slip on the coating surface, lowering the force required for fouling-release.[12] Tensile modulus was measured on dumbbell shape coating films and all the coatings showed a modulus within a very narrow range of 0.8–1.7 Mpa, as shown in Figure 3.

Resistance and release performance of coatings with respect to barnacles was determined using a static immersion test in the Indian River Lagoon. The performance of coatings against barnacle settlement and adhesion was compared with that

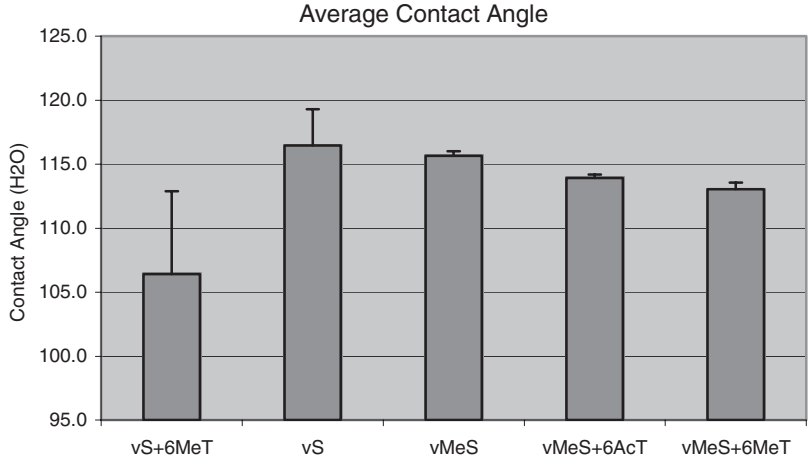

Figure 2.
Water contact angle for the coatings produced.

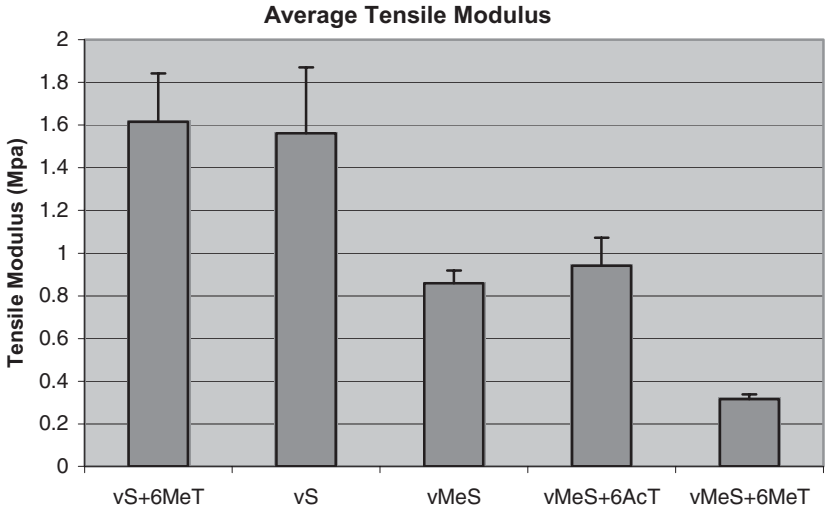

Figure 3.
Average Tensile Modulus measurement on coating samples.

of a commercial copper oxide-based antifouling coating and the commercial fouling-release coating, Intersleek 425.

After 29 days of water immersion, the results showed that the coatings based on AcT significantly reduced macro-fouling and the performance was close to that of the Cu ablative coating (Figures 4 and 5). Interestingly, the antifouling performance of the coatings based on MeT was not significantly better than the coatings containing no biocide moiety. Although both vS and vS+6MeT have higher tensile modulus, their antifouling performance was similar to the performance of all the other coatings except vMeS+6AcT. Thus, it appears that the impact of coating tensile modulus on antifouling performance is insignificant for this particular example.

This result is inconsistant with results previously described that suggest there is a relationship between modulus and antifouling performance for siloxane-based, antifouling coatings.[13] However, it may be that the modulus effect is only observed when the modulus difference is a order of magnitude. At 29 days of water immersion, barnacle adhesion was not measured because there were not enough barnacles settled on the coating surfaces to obtained good statistics.

After 85 days of water immersion, all coating panels were evenly covered by barnacles except for the Cu reference

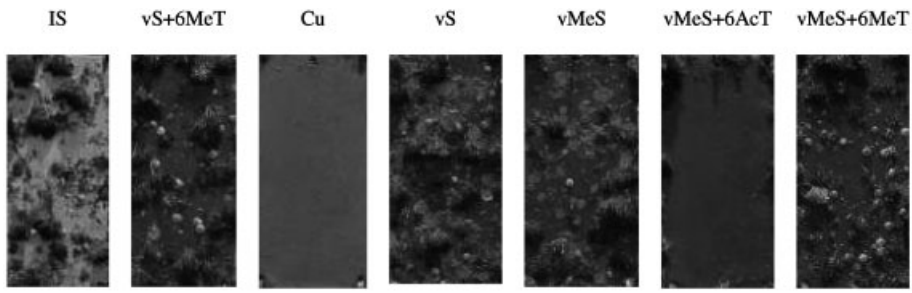

Figure 4.
Photos have been take after 29 days of static immertion at Indian River Lagoon (Melbourne, FL).

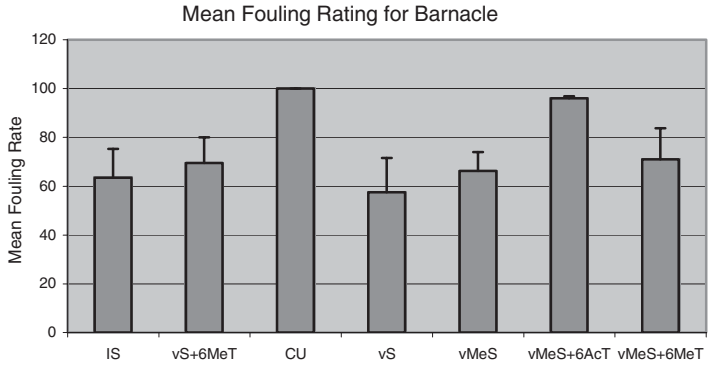

Figure 5.
Mean fouling rating for barnacle after 29 days of static immertion at Indian River Lagoon (Melbourne, FL).

coating, as shown in Figure 6. At 85 days of water immersion, there was no observation of antifouling character for coatings based on either AcT or MeT. This result indicates that the tethered triclosan moieties only provide antifouling character for a relatively short period of time for the levels of AcT investigated. In the future, it will be necessary to determine the relationship between the effective time period and tethered triclosan concentration in the coating matrix.

Average barnacle adhesion strength was measured according to ASTM D5618-94 using a shear force gauge and the results obtained are shown in Figure 7. From Figure 7, it can be seen that all of the coatings containing AcT or MeT showed higher adhesion than the non-biocidal coatings. Also, coating vS+6MeT showed significantly higher barnacle adhesion than vMeS, IS, vS, and vMeS+6AcT. It is currently not clear why the coatings containing MeT showed significantly higher barnacle adhesion. But, it is clear that attachment of Triclosan moieties to the coating matrix through the derivative, MeT, did not provide any benefit to antifouling performance or fouling-release performance.

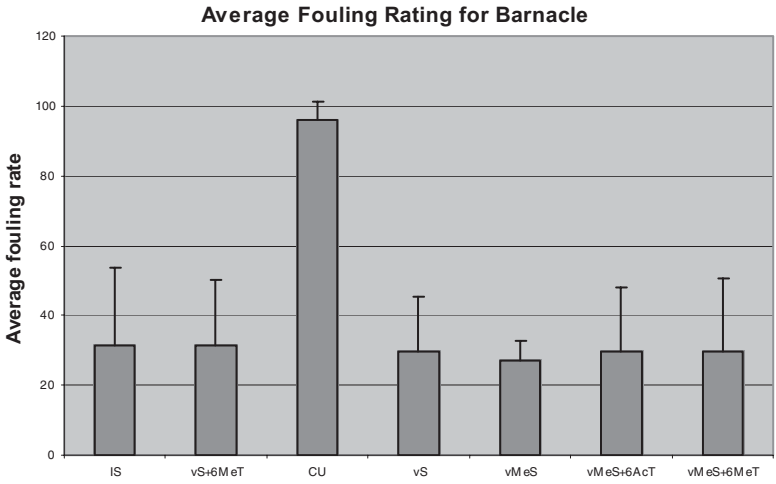

Figure 6.
Mean fouling rating for barnacle after 85 days of static immertion at Indian River Lagoon (Melbourne, FL).

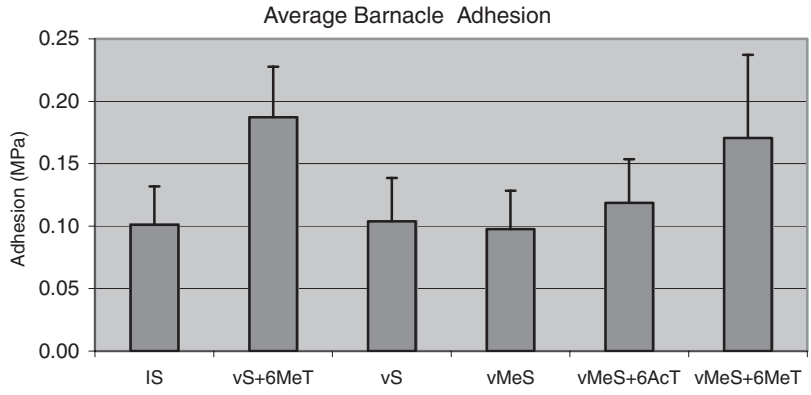

Figure 7.
Average adhesion strength measurement using the shear force gauge. The shear strength was calculated from the shear force measured divide by area of barnacle base plate mark on coating surface.

However, the use of AcT to attach the Triclosan moiety to the coating matrix clearly showed significant antifouling activity at least for the early stage of immersion and the fouling-release capability was comparable with the fouling-release reference coating, Intersleek 425.

Conclusion

The preparation, characterization, and ocean-site immersion testing of biocide incorporated silicone coatings for marine applications have been conducted. In contrast to historical R&D approaches, our approach was to design coatings that possess both non-leaching/non-metallic biocidal elements and foul-release elements into the same coating. Derivatives of the biocide, Triclosan, were used to covalently attach the biocide moiety to a silicone backbone using hydrosilation. The static immersion studies showed that the coatings with covalently linked biocide and the appropriate physical characteristics are effective in preventing macrofouling. In addition, the biocidal effectiveness was found to be time dependent and further studies should be conducted to determine the relationship between the effective antifouling time period and tethered triclosan concentration in the coating matrix.

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