Non-Leaching, Benign, Fouling Control, Multilayer Polymer Coatings for Marine Applications: PP-1274 Findings

Christopher K. Ober
Cornell University
Materials Science and Engineering Department
310 Bard Hall
Ithaca, NY 14853, USA
E-mail: cober@ccmr.cornell.edu
Phone: 607-255-8417
Fax: 607-255-6575

SEPTEMBER 2003

CONTENTS

Acronyms……. 3

Executive Summary……. 4

Background…….. 5

Approach……..6
Polymer Synthesis and Processing…….6
Surface Characterization……6

Materials and Methods…… 7
Materials…… 7
Synthesis of Poly(styrene-*block*-isoprene) and Hydroxylation……. 8
Bromination of Poly(ethylene glycol) and Hydroxylated Block Copolymer…… 8
Attachment of Poly(ethylene glycol) Side Groups to Block Copolymer…….. 8
Block Copolymers with Semifluorinated Side Groups……. 8
Characterization of the Surface-Active Block Copolymers……...8
Algal Zoospore Attachment Assays…….. 9
Pseudobarnacle Adhesion…….. 10

Results……. 11
Polymer Synthesis……. 11
Surface Studies…….. 12
Zoospore Attachment and Release…… 14
Pseudobarnacle Adhesion…….. 15

Discussion……18

Transition Plan……19

Conclusion……... 20

Recommendations……20

List of Publications…….. 21

ACRONYMS

NEXAFS	near-edge X-ray absorption fine structure
NSWCCD	Naval Surface Research Warfare Center, Carderock Division
ONR	Office of Naval Research
PEEM	photoemission electron microscopy
PEG	poly(ethylene glycol)
PEY	partial electron yield
PI	polyisoprene
PS	polystyrene
PS/PI	poly(styrene-*block*-isoprene)
PS/PI Br	poly(styrene-*block*-isoprene) with brominated isoprene block
PS/PI Br-F8H6	PS/PI Br polymer modified using $F(CF_2)_8(CH_2)_6OH$
PS/PI OH	poly(styrene-*block*-isoprene) with hydroxylated isoprene block
PS/PI OH-PEG164	PS/PI OH polymer modified using 164 g/mol PEG
PS/PI OH-PEG550	PS/PI OH polymer modified using 550 g/mol PEG
PTFE	poly(tetrafluoroethylene)
SABC	surface active block copolymer
SEBS	styrene-ethylene/butylene-styrene
SF	semifluorinated
SFM	scanning force microscopy
T_g	glass transition temperature
TBT	tributyltin
THF	tetrahydrofuran
TPE	thermoplastic elastomer

EXECUTIVE SUMMARY

The goal of this research is to produce environmentally friendly coatings that protect the hulls of ships below the waterline against fouling by seaweed, barnacles, and other organisms. Fouling by these organisms produces additional drag on the ship, increasing the operating and maintenance costs. Currently, antifouling paints containing tin and copper biocides are used because of their effectiveness against most forms of fouling. However, these biocidal organometallic compounds that are environmentally persistant cause damage to the ecosystem, and enter the food chain. The ban on tributyltin (TBT) antifoulants by the International Maritime Organization will be effective in 2008, and copper-based coatings are expected to face similar restrictions in the near future. Non-toxic "fouling-release" or "fouling-repellant" coatings are the desirable alternatives to coatings that are biocidal. Silicone-based paints that belong to the former category are commercially available, but do satisfy many of the desired performace characteristics. The soft silicones do not withstand the rigorous demands of the marine environment, do not sufficiently and consistently self-clean, or, due to polymer restructuring or other degradation pathways, lose many of the desirable surface properties with time and exposure to marine organisms.

This report describes the synthesis and testing of block copolymers that contain semifluorinated (SF) and poly(ethylene glycol) (PEG) side groups, and show promise as non-toxic, antifouling substitutes to copper-containing paints. These surface-active groups modify the coating-water interfacial energy, conferring fouling-release or fouling-repellant properties to the surface. Fouling-release also depends on the elastic modulus of the surface, which can be controlled by blending the surface-active block copolymers (SABC) with a commercially available thermoplastic elastomer (TPE) such as the Kraton® styrene-ethylene/butylene-styrene (SEBS) triblock polymer. The resulting coatings could be either a single layer obtained from a blend of the TPE and SABC, or a bi-layer with an elastomeric base (TPE) and an upper surface-active layer (SABC). The latter approach will be described in this report.

Semifluorinated and PEG containing block copolymers were synthesized. These materials were coated via a newly developed spray coating process onto SEBS-coated aluminum panels for pseudo-barnacle adhesion testing. Results from the first batch of panels indicated that SF polymers have better adhesion reduction properties than the PEG materials (in the dry state). Due to heterogeneous surface morphology of the coatings and concerns about the molecular-weight incompatibility of the styrene blocks in the SABC and SEBS, new panels were prepared with lower molecular-weight polystyrene blocks in the SABC. However, the new panels showed inferior performance to the first batch. We believe that modifications of the process will lead to more uniform coatings that will successfully provide for fouling release.

BACKGROUND

Marine fouling is a major problem in the transport of materials worldwide as it raises fuel consumption by as much as 30 %. It is hoped that the approach of lowering the strength of adhesion between the fouling organisms and the surface, will present environmentally friendly coatings that not only decrease the accumulation of the organisms, but also aid their removal. The diversity of fouling organisms and environmental conditions world-wide makes the task of developing a coating that resists fouling and/or self-cleans challenging, and novel non-toxic solutions are urgently needed.

Current understanding of antifouling materials is that the most effective copper-free fouling control systems are low surface energy coatings, namely silicone or fluoropolymer based coatings that minimize the adhesion strength between fouling organisms and surface. For extended performance life, these coating systems must have controlled and stable surface energy and composition, have elastomeric properties, and adhere well to the substrate. To date, several fouling release (FR) coating systems are commercially available, mostly based on silicone polymers, yet none meet all of the desired performance characteristics. Many lack the toughness required to withstand the rigorous physical demands of the marine environment, do not sufficiently and consistently self-clean, and due to polymer re-structuring or other degradation pathways, lose many of the desirable surface properties with time and exposure to the marine environment.

It is now apparent that adhesion strength of hard fouling organisms is proportional to $(\gamma E)^{1/2}$, where γ is the surface energy and E is the modulus of the surface. For this reason, silicone elastomers are, as of now, the only commercial environmentally benign fouling release coatings, because they possess both low modulus and low surface energy. The efficacy of silicone polymers is lower than that of biocide-containing antifouling paints, and regular mechanical cleaning (scrubbing) of the coated surface is required adding to the operating expense. It would be advantageous to use fluorinated materials to lower the surface energy of a coating and decrease the adhesion strength, but these materials are typically hard and brittle with high moduli and do not provide good control of biofouling. Thermoplastic elastomers such as styrene-ethylene/butylene-styrene (SEBS) block copolymers offer good mechanical properties (low E), but not the desired surface energy. A method to incorporate both the properties, by blending styrene-ethylene/butylene-styrene (SEBS) thermoplastic elastomers with surface-active block copolymers (SABC), is expected to offer good fouling control. However, the hydrophobic, fluorinated surfaces often undergo rapid molecular reconstruction at the surface in polar environments, such as water, and lose their fouling release characteristics. This makes the creation of fluorinated, fouling-release surfaces that do not reconstruct a challenge. Several approaches toward the creation of stable surfaces have been examined, and of particular interest is the stabilization of the surface with liquid crystalline semifluorinated groups (short segments of alkyl and perfluoroalkyl groups of 5-10 carbons each). It was anticipated that assembly of such groups onto a surface would result in stable fouling-release surfaces.

Poly(ethylene glycol) (PEG) is commonly known by the biomaterials community to have good fouling resistance. The polymer has many useful properties such as low protein adsorption, good stability, low toxicity, and is, in general, compatible with biological processes as well as the human body. For fouling-release applications, such materials are lacking in several critical

properties such as mechanical behavior, long-term stability, and ease of application, which limits their use as coating materials. As with biomedical surfaces used in the body, the first event in biofouling in the marine environment is adsorption of a conditioning film that includes proteins and glycoproteins. It was hypothesized that incorporation of PEG into a coating system, would prevent protein adsorption, thereby reducing the adhesion of such organisms. Both semifluorinated and PEG containing coatings were synthesized. The performance of these coatings was investigated, the results providing a direction toward improved systems for fouling release that mitigate the use of toxic organocopper antifoulants.

APPROACH

Polymer Synthesis and Processing

Surface-active block copolymers were prepared by polymer analogous reactions on poly(styrene-b-isoprene) block copolymers (PS/PI). The PS/PI polymers were synthesized by anionic polymerization in tetrahydrofuran (THF) at −78 °C, and *n*-butyllithium initiator, resulting in pendent vinyl groups in the isoprene blocks. The vinyl groups were converted to hydroxyl groups, by hydroboration chemistry using 9-borabicyclo[3.3.1]nonane, followed by oxidation using sodium hydroxide and hydrogen peroxide. The hydroxyl groups on the polymer were used to attach either perfluoro alcohols, e.g. $F(CF_2)_8(CH_2)_6OH$, or PEG, e.g. $CH_3(OCH_2CH_2)_{12}OH$, to the polymer backbone via etherification chemistry giving the surface-active block copolymers.

The coatings were prepared by casting solutions of the TPE and SABC in toluene, on the substrate. A film of the SABC was cast on a film of the SEBS elastomer using one of several methods, and the bilayer annealed at a temperature above the glass transition temperature of the PS block (ca. 100 °C). (The thermoplastic SEBS helps the anchoring of the coating to the substrate. The lower SEBS layer contains domains of micellized polystyrene blocks of the TPE in the ethylene/butylenes copolymer matrix.) Thermal annealing of the bilayer coating anchored the SABC to the SEBS layer by interpenetration of the PS block of the SABC chains into the PS domains of the SEBS. This improves adhesion of the SABC layer to the SEBS and prevents leaching of the coating into the sea-water. Using this approach, only a small quantity of the surface active polymer was required for the desired coating performance.

Surface Characterization

The surface energy of the coatings was quantified by determining the dynamic (advancing and receding) contact angles of water drops on these surfaces. To determine the extent of surface reconstruction upon prolonged exposure to sea water, the contact angle of an air bubble adhering to the substrate submerged in water was measured using the captive air bubble method. The surface morphology and chemical composition of the coatings was characterized using Atomic Force Microscopy (AFM), and Near-Edge X-Ray Absorption Fine Structure (NEXAFS).

The semifluorinated (SF) side groups in the SABC self-assemble to form liquid crystalline domains on the surface. Furthermore, if the order-to-disorder transition temperature of the liquid crystalline arrangement is above ambient temperature, restructuring of the surface upon exposure to water can be avoided. We have designed polymers to take advantage of this feature. NEXAFS is a surface spectroscopy technique that was used to probe the chemical composition within the top 2 nm of the surface. NEXAFS was also used to determine the orientation of molecules at the surfaceThese experiments involve the X-ray excitation of a carbon K shell electron to an unoccupied low-lying antibonding σ^* or π^* molecular orbitals. Because sharp core level excitations for C and F occur in the soft X-ray region, NEXAFS is an effective technique for probing molecular orientations of the SF side groups in the SF polymers.

AFM was used to probe the local mechanical properties and chemical composition of the SABC/SEBS surface, as these are expected to greatly influence the fouling release properties of the surface. Tapping mode AFM technique were employed, using different amplitudes of the cantilever oscillation. At very low amplitudes ("light tapping") the three-dimensional topography of the surface was imaged. At higher amplitudes, ("hard tapping") hard structures beneath soft surfaces become discernable. These analyses were carried out at different temperatures. For such advanced AFM measurements we have access to a new generation of scanning force microscopes under development at Digital Instruments, through our collaboration with Dr. Sergei Magonov.

Testing of the fouling release properties of these coatings is an important part of this program. Test coatings with good adhesive and mechanical properties were prepared on large-scale plaques. These plaques can be easily accommodated since the bulk of the coating is based on the commercially available SEBS. New coating methods were developed including those based on spray coating. Laboratory and marine testing of the coatings for biofouling adhesion, fouling control, and physical property evaluation, was carried out in conjunction with Elizabeth Haslbeck of the Naval Surface Warfare Center, Carderock Division (NSWCCD). Leveraging the ONR program, testing of these coatings on microscope slides for settlement and release of *Entermorpha* was performed in the laboratory of Maureen Callow (University of Birmingham UK), through our participation in the Office of Naval Research program on antifouling coatings.

MATERIALS AND METHODS

Materials

Tetrahydrofuran (THF) was distilled from a sodium/benzophenone complex under nitrogen. Alexafluor 488 conjugated type IV human placental collagen (cat. no. C-13185) and Alexafluor 488 conjugated polyclonal rabbit IgG (cat. no. A-11090) were purchased from Molecular Probes. BSA (A-40503 lot# 10K0888) and fibronectin (F4759 lot# 100K7620) were purchased from Sigma and labeled using Alexafluor 488 succinimidyl ester (molecular probes catalog # A-10235). All proteins had dye to protein ratio of between 4.5 and 5. Elastomeric styrene-ethylene/butylene-styrene (SEBS) G1562M was donated by Kraton. All other reagents purchased from Aldrich and were used without further purification unless otherwise mentioned.

Synthesis of poly(styrene-*block*-isoprene) and hydroxylation

Poly(styrene-*block*-isoprene) polymers with PS molecular-weight of 25,000 g/mol or 8,000 g/mol, and polyisoprene molecular-weight of 15,000 g/mol and 1,2- and 3,4-addition content greater than 97% were synthesized (polydispersity of 1.05). These polymers were subjected to hydroboration-oxidation reaction to yield the corresponding hydroxylated diblock copolymers with an extent of conversion of approximately 99%. Details of the experimental conditions for the polymer modification procedure are given below.

Bromination of poly(ethylene glycol) and hydroxylated block copolymer

Brominations were carried out on the methoxy terminated poly(ethylene glycol) of molecular-weights 164 g/mol and 550 g/mol. Three mmol PEG-OH and 3.5 mmol carbon tetrabromide dissolved in 2 ml methylene chloride (CH_2Cl_2) was cooled to –20 °C. A solution of 4.0 mmol triphenylphosphine dissolved in 2 ml CH_2Cl_2 was added dropwise while stirring. The solvent was evaporated off and the solid was extracted with water. After drying and filtering, a clear, viscous, yellow oil was produced. Bromination of polymer was achieved in a similar manner: 0.5g PS/PI-OH (3.0 mmol hydroxyl) and 3.5 mmol of carbon tetrabromide were dissolved in 5ml of THF cooled to –20 °C. Four mmol triphenylphosphine in 2 ml THF were added dropwise. The solution was filtered, precipitated and filtered once each into methanol and hexanes. A pale yellow rubbery polymer was recovered (PS/PI-Br) and was found to be brominated to over 99 %.

Attachment of the poly(ethylene glycol) side groups to block copolymer

In a typical polymer side-chain modification reaction, 0.88 mmol hydroxyl groups of the hydroxylated block copolymer (PS/PI-OH) was dissolved in 2 ml anhydrous THF and either 0.3 ml PEG164-Br or 1.0 ml PEG550-Br. Seventy mg sodium hydride was added and the reaction was left stirring for 48 h. The solution was precipitated into water and after filtering was precipitated again into methanol. The recovered polymers were a pale yellow elastic material with side-chain attachment between 55 % and 70 %.

Block copolymers with semifluorinated side groups

The brominated polymer was refluxed with about 100 % molar excess of semifluorinated alkoxylate in the presense of 18-crown-6 catalyst in methylene chloride overnight. To form the alkoxylate, the semifluorinated alcohol was stirred with an equimolar amount of potassium *t*-butoxide at 50 °C for 1 hour. Polymers were recovered and purified by precipitation in methanol twice. More than 70 % of the bromine groups on the polymer backbone were found to be substituted by the SF side groups.

Characterization of the surface-active block copolymers

^{1}H-NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Infrared spectra were obtained using a Mattson on a 2020 Galaxy Series FTIR spectrometer. Contact angle values were determined using the captive air bubble technique in a custom-built sample

holder, distilled water, Gilmont syringe, and Ramé-Hart telescopic goniometer. Samples were soaked in distilled water for 1 h prior to measurement of contact angles. An average of at least ten different individual measurements was used. The NEXAFS experiments were performed using the Dow/NIST U7A beamline at the Brookhaven National Laboratory. Atomic Force Microscopy was performed at University of California at Santa Barbara.

Algal zoospore attachment assays

The attachment of marine algal zoospores was carried out on bilayer polymer films prepared by solvent casting 15 wt-% solution of SEBS in toluene, onto glass microscope slides (76 mm × 25 mm) and annealing under vacuum at 120 °C for 15 h. The surface active block copolymers were spin-coated onto the SEBS primer, using a 0.3 wt-% solution of the polymer in toluene, and dried under vacuum at 120 °C for 15 h.

Fertile plants of *Enteromorpha linza* were collected from Wembury Beach, England ($50^{o}18'$ N, $4^{o}02'$ W). Zoospores were released and prepared for attachment experiments. Ten ml aliquots (1.5×10^{6} spore ml^{-1}) were pipetted into individual compartments of polystyrene culture dishes (Fisher), each containing a glass microscope slide. Six replicate dishes were incubated in the dark for ca. 1 h before the slides were washed by passing backward and forward ten times through a beaker of sea-water, in order to remove unattached spores. Three replicate slides from each treatment were fixed in 2 % glutaraldehyde in seawater and processed. The remaining three replicates were placed in a flow apparatus and exposed to a fully-developed turbulent flow for 5 min. After fixing the slides in 2 % glutaraldehyde, the adhered spores were visualized by autofluorescence of chlorophyll, and quantified by image analysis. Thirty counts were taken at 1 mm intervals along the middle of the long axis of each of the three replicate slides. Means and 95 % confidence limits were calculated, and expressed as the mean number of attached spores per square millimeter of the surface. The mean number of spores remaining attached to the surface after exposure to turbulent flow was compared with the mean number before the slides were subjected to flow. Ninety-five percent confidence limits were calculated from arc-sine transformed data.

Figure 1 shows a schematic of the experiment.

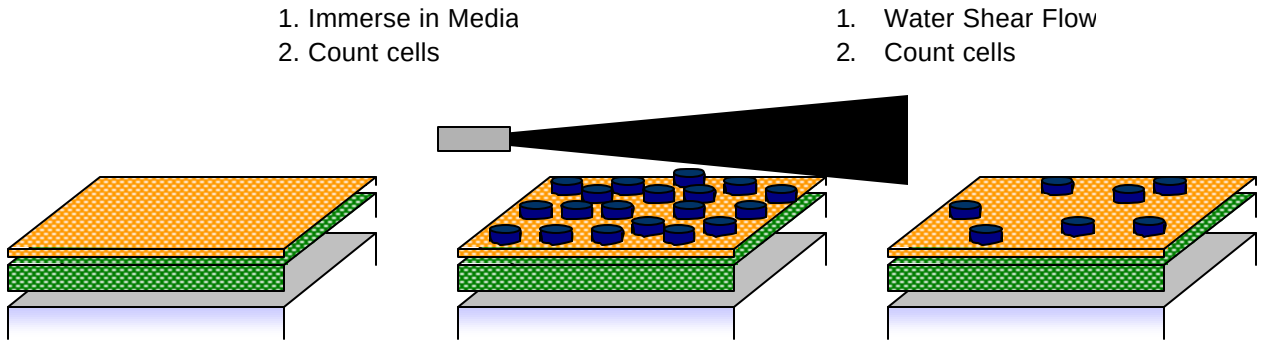

Figure 1. Schematic of the experiment for determining the extent of zoospore settlement and removal.

The turbulent flow-apparatus, and a glass slide covered with the sporelings is shown in **Figure 2** (from Maureen Callow, University of Birmingham).

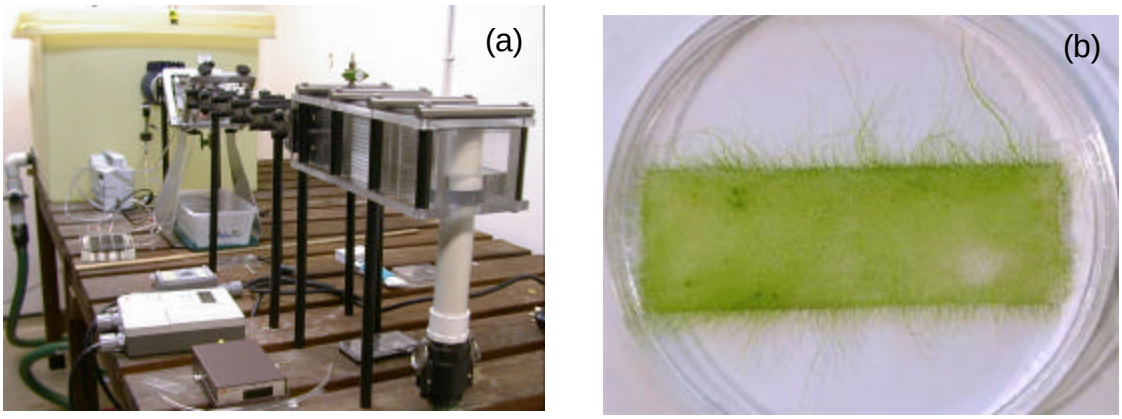

Figure 2. (a) Turbulent flow apparatus for biofouling removal assays; (b) a microscope glass slide covered with sporelings.

Pseudobarnacle adhesion

Bilayer coatings were prepared by coating aluminum panels with epoxy resin, and curing to a tack free finish. Epoxy was then re-applied and cured until tacky, when a solution of maleic anhydride containing SEBS (Kraton® FG1901X) in toluene, was sprayed on the surface, and dried. Prior to applying the final coat, a fresh layer of the regular SEBS (Kraton® G1562M), was applied by spray-coating from 12.5% toluene with a crafts-style air-brush using compressed nitrogen at 30 psi, and dried. **Figure 3** shows the device used for spray-coating. Back and forth spraying was done such that the entire panel was wetted from a distance of approximately 6 inches and the edge of each pass overlapped with the previous pass. After air drying until no odor of toluene was evident, the panel was rotated by 90 degrees clockwise and sprayed as before. After 4 coatings the panel was dried overnight in air. The final top-coating of the surface-active block copolymer was spray coated to approximately 200 nm thickness from toluene (SF side-chains) or chloroform (PEG side-chains) and the panels were annealed in either vacuum at 120 °C in the case of SF side-chains, or under water for 1 hour in the case of PEG side-chains. Final SABC topcoat was applied in a similar method by weighing out a pre-determined amount of material into the well, diluting with an appropriate solvent, and coating as before until the ink well went dry. The SABC thickness was estimated from amount deposited (using only the weighed amount in the well), density, and area of the panel. This overall procedure ensured good adhesion to the test panels. Pseudobarnacles were attached to the surface with epoxy and pulled straight off with a force gauge with a limit of 20 pounds of force.

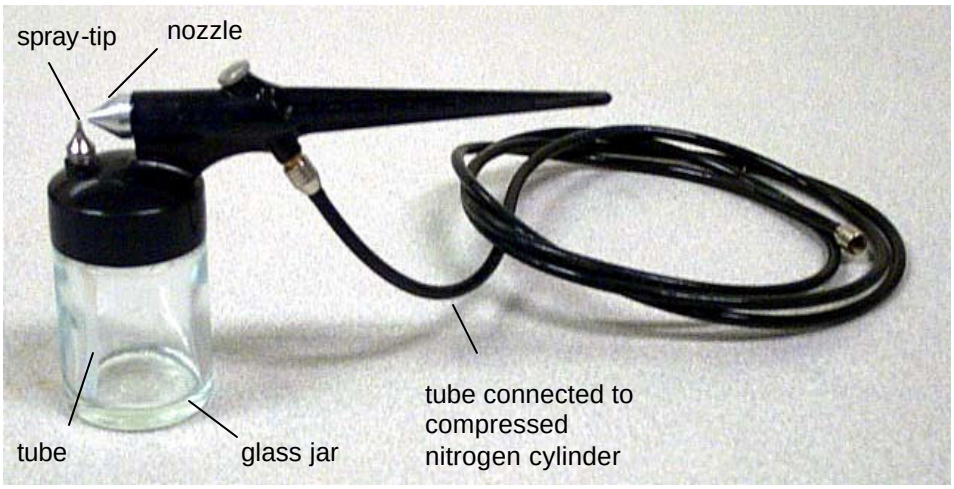

Figure 3. Device for spray-coating (Badger Model 250, single-action, external-mix, siphon-feed airbrush). The polymer solution is taken in the glass jar, and reaches the spray-tip by air suction. The solution is atomized by a pressurized nitrogen-stream flowing through the nozzle upon pressing the button on the nozzle. The degree of atomization is controlled by the air pressure and the coating viscosity. The width of the spray can be adjusted (from ¾ in. to 2 in.) by raising or lowering the spray tip.

RESULTS

Polymer synthesis

The overall procedure for the synthesis of the PEG containing and SF side-chain block copolymers is shown in **Figure 4**. After each step, the reaction was followed by FTIR spectroscopy, and the extent of substitution of the isoprene side-chains of the parent block copolymer was determined by ^{1}H-NMR spectroscopy.

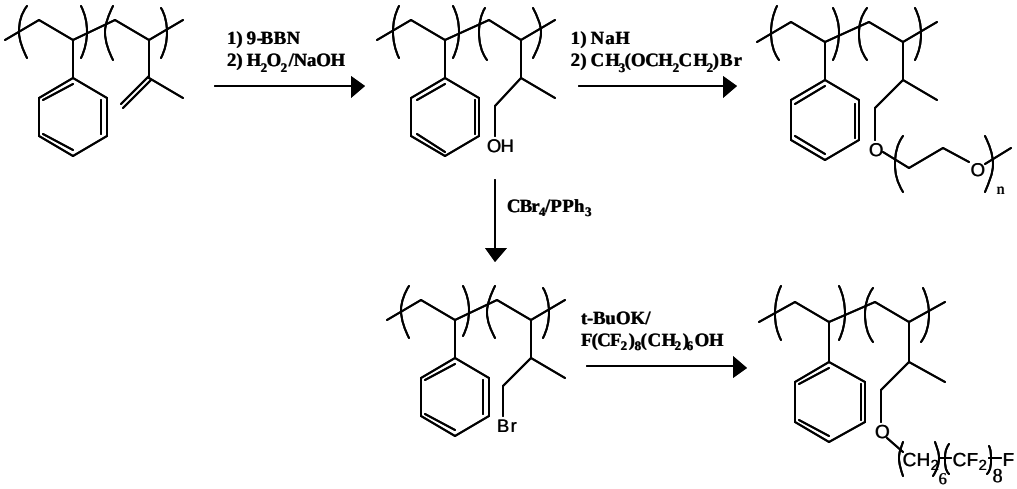

Figure 4. Preparation of the surface-active block copolymers (SABC).

Surface studies

Typical dynamic contact angle measurements showed a significant difference in the advancing and receding contact angles (hysteresis). The advancing contact angles of a captive air bubble are given in **Table 1**.

Table 1. Under-water static contact angles of bilayer coatings

Sample	q **(degrees)***
SEBS	76 ± 4
Polystyrene	70 ± 2
PS/PI(25/15)Br-H6F8	90 ± 4
PS/PI(25/15)OH-PEG164	58 ± 3
PS/PI(25/15)OH-PEG550	74 ± 9

*Underwater contact angles were determined after 1 h immersion. Values shown are the mean and standard deviation from 10 replicate measurements.

The effect of the SABC on the surface is clearly evident. The SEBS primer had an advancing contact angle of 76°, while the SEBS surface modified with semifluorinated SABC [PS/PI(25/15)Br-H6F8] had an advancing contact angle of 90°, indicating an enhanced hydrophobic nature. However, upon modification with the PEG containing SABC, viz. PS/PI(25/15)OH- PEG164, the contact angle was lowered to 58°. PS/PI(25/15)OH-PEG550 coated SEBS bilayers had a value not significantly different to the SEBS base. For reference, polystyrene has been included in **Table 1** and, predictably, has a value of ca. 70°, just below that of SEBS.

NEXAFS studies of the SABC with SF side groups show that only a small amount of PS is present at the surface, as indicated by the relatively low intensity of the 1s → π^* transition peak of the PS phenyl ring at 284.5 eV. The NEXAFS experiments were carried out at eight different orientations of the sample with respect to the incident X-ray beam, θ, (θ = 20, 30, 40, 55, 60, 70, 80, and 90°). As can be seen from **Figure 5**, the intensity of the 1s → σ^* transition associated with the C–F bond (E = 292.0 eV) showed an angular dependence, which indicates ordering of the SF side groups at the surface.

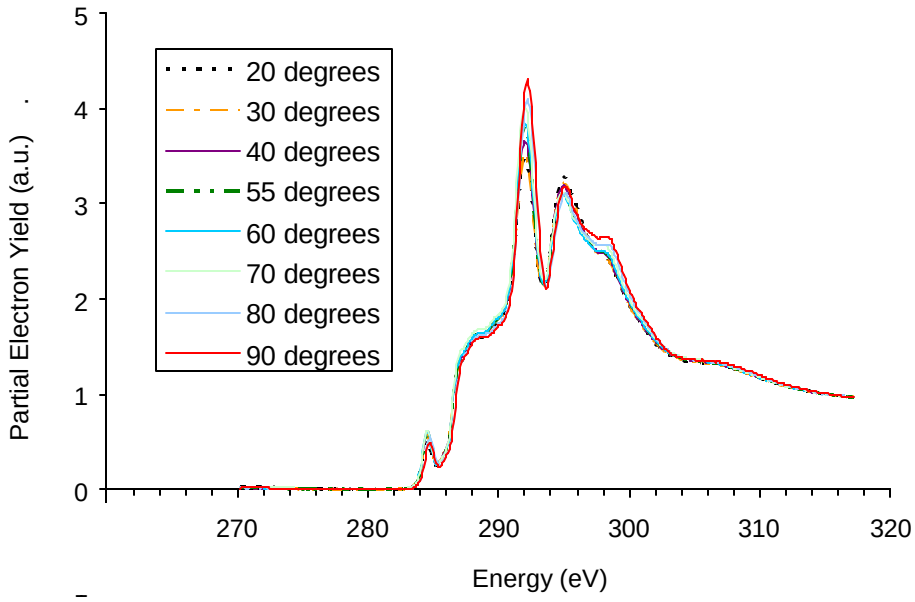

Figure 5. Representative angle dependent NEXAFS spectra of SABC with SF side groups.

Figure 6 shows the AFM phase-image of the fluorinated SABC surface. The image shows that the surface is not uniformly covered with the SF surface-active block copolymer. In fact, the SABC forms domains on the surface, and the lower SEBS layer is exposed in regions where SABC domains are not present. This result and others obtained on the sample show that the newly developed spray coating method did not completely coat the SEBS base layer and needs further improvement.

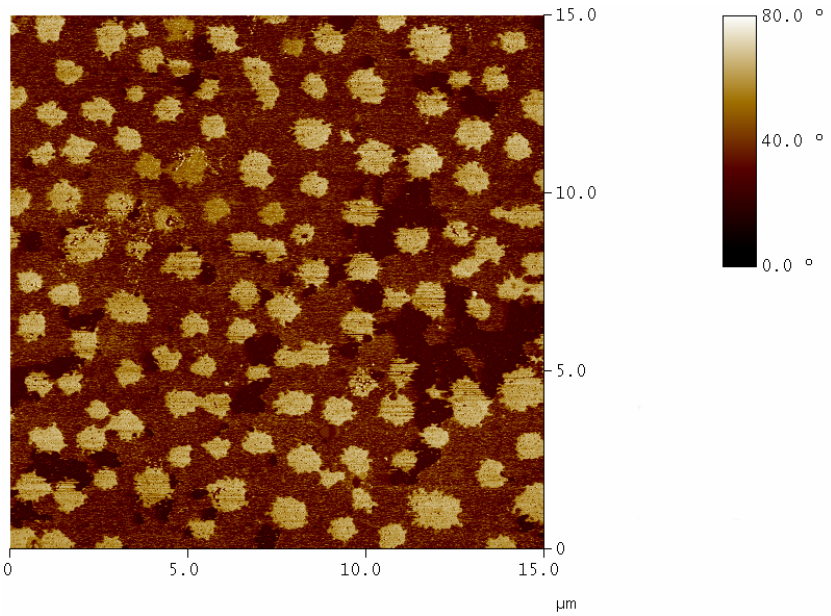

Figure 6. Representative AFM phase-image of a coating containing SABC with SF side groups.

Zoospore attachment and release

The number of spores that settled on glass was about two times higher than the settlement on the other surfaces (cf. **Figure 7**).

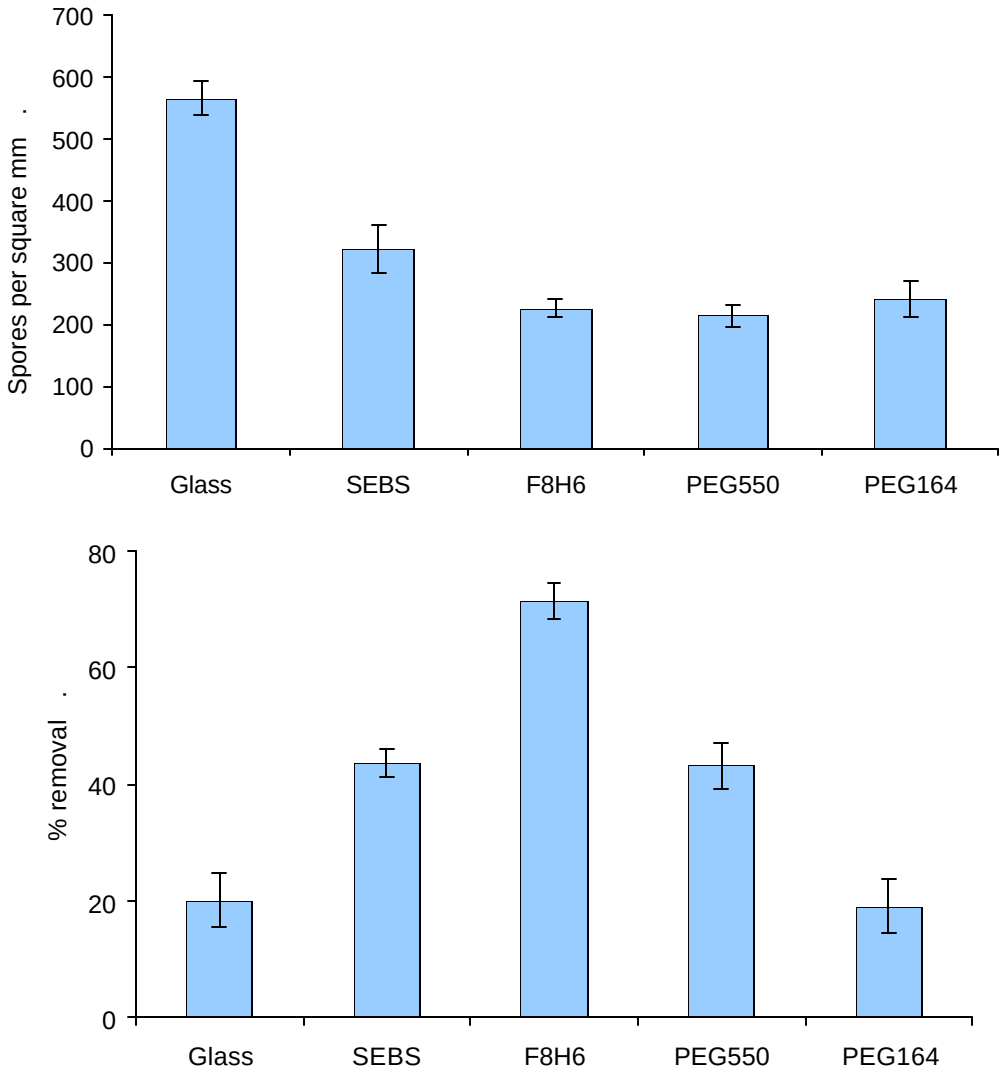

Figure 7. *Enteromorpha* zoospore settlement (top), and release after applying 55 Pa shear stress of turbulent water stream (bottom), from the coatings. All polymers were prepared starting from PS/PI block copolymers with block molecular-weights of 25,000 g/mol and 15,000 g/mol, respectively. F8H6, PEG550 and PEG164 represent the surface-active block copolymers PS/PI Br-F8H6, PS/PI OH-PEG550 and PS/PIOH-PEG164, respectively.

One-way ANOVA showed that the settlement on glass and the SEBS base were significantly different from each other and also from all the other coatings. There were significant differences in the adhesion strength of settled zoospores on the four surfaces. The greatest release was from the fluorinated PS/PI(25/15)Br-H6F8 coating. Approximately 70% of the spores were removed from this coating compared to only ca. 20 % and 40 %, respectively, from glass and the SEBS

surfaces. One-way ANOVA on arcsine-transformed data revealed no difference between glass and PS/PI(25/15)OH-PEG164, and between the SEBS base and PS/PI(25/15)OH-PEG550. Thus the major part of the research program focused on these types of surfaces.

Sporeling settlement (that is, study of the more fully developed Entermorpha spores) was also used to assess biofouling. **Figure 8** shows the appearance of the glass slides covered with the bilayer coatings prepared using SABCs of different molecular weights, after the sporeling removal assays. It is clear that the removal of sporelings upon exposure to a turbulent shear stress of 55 Pa, is better (in certain regions of the slides) on the surfaces coated with the SABC, when compared to glass or SEBS surfaces. Thus we have developed materials that show promise, provided the coating process can be optimized.

Figure 8. Results of sporeling removal assays on glass microscope slides coated with the SF and PEG containing SABCs of different molecular weights. 3 % and 0.3 % indicate the weight concentrations of the solutions of SABC used for spin-coating.

Pseudobarnacle adhesion

Panels were tested at Carderock by Haslbeck and coworkers and on the whole, less than satisfactory results were obtained. All PEG containing coatings showed high pull-off forces (cf. **Table 2**), as expected from the high surface-energy of the coatings in the dry state. In the case of the semifluorinated coatings, the pull-off force was lower, as also could be expected. However, the panels were not uniform in release behavior, with significant deviation in the pull-off force in

different regions of the panel, as shown in **Figure 9**. Pull-off forces ranged from excellent to unsatisfactory.

Table 2. Mean force gauge values for pseudobarnacle pulloff [a]

Sample	Force (lbs)
SEBS	20
PEG164 [b]	20
PEG550 [b]	20
F8H6 [b]	7
PEG550 [c]	20
F8H6 [d]	20

[a] PEG164 and PEG550 indicate the PEG side groups with molecular-weights of 160 g/mol and 550 g/mol; F8H6 denotes the semifluorinated side group corresponding to $F(CF_2)_8(CH_2)_6OH$.
[b] SABC prepared using PS/PI block copolymer, with PS and PI block molecular-weights of 25,000 g/mol and 15,000 g/mol, respectively.
[c] PS and PI block molecular-weights of 8,000 g/mol and 4,000 g/mol, respectively
[d] PS and PI block molecular-weights of 8,000 g/mol and 16,000 g/mol, respectively

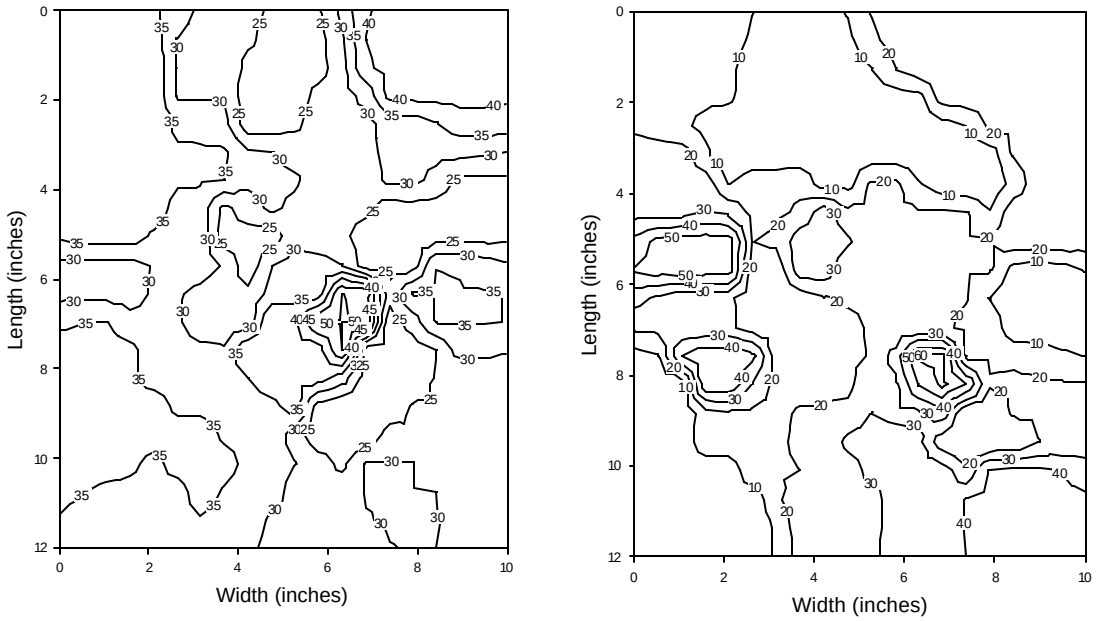

Figure 8. Contour plots of pull-off pressure (psi) of pseudobarnacles on semi-fluorinated bilayer coatings (prepared starting from PS/PI block copolymer with 25,000 g/mol and 15,000 g/mol PS and PI blocks).

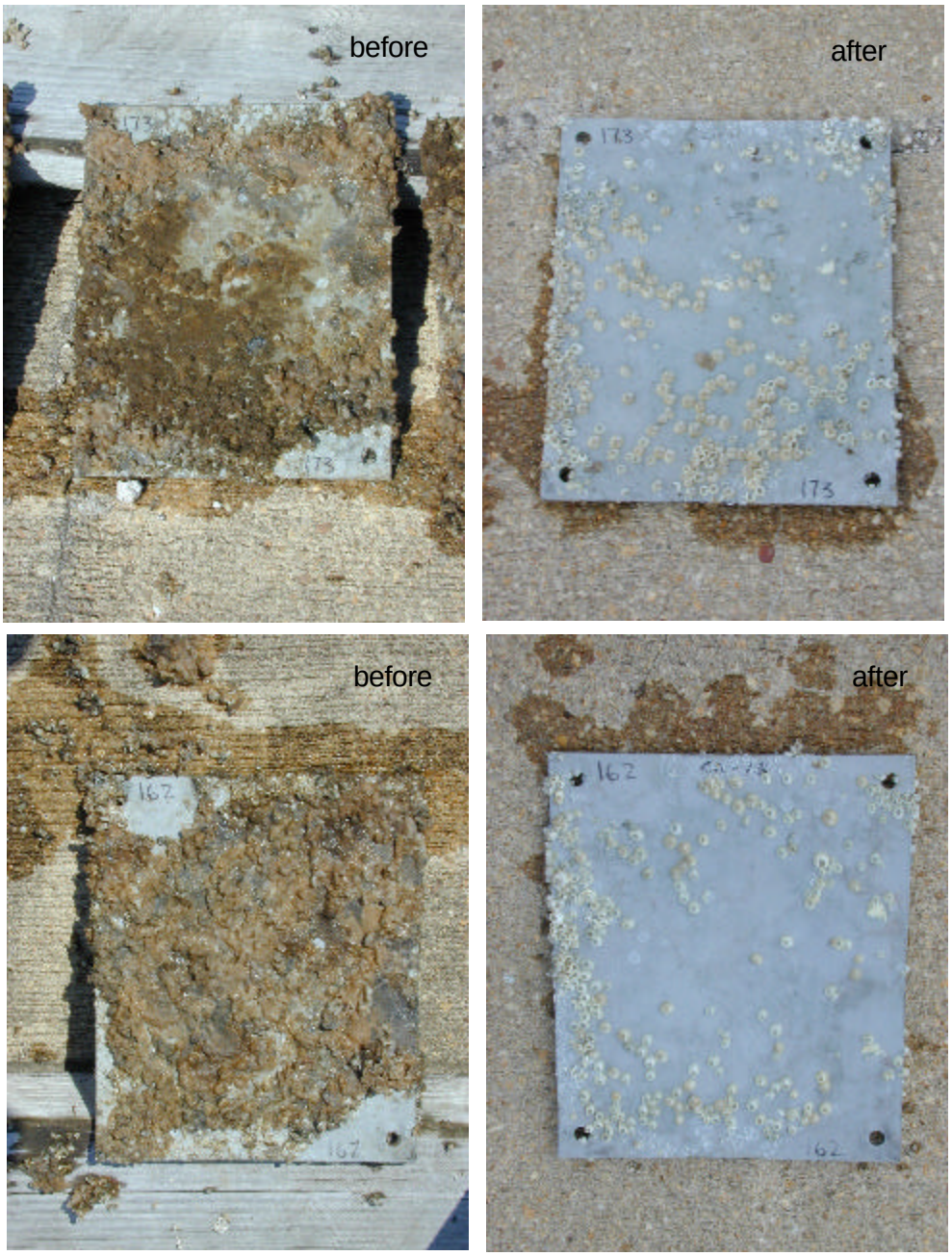

Figure 9. Plaques covered by PEG containing SABC: PS/PI(25/15)-PEG164 (top), and PS/PI(8/4)-PEG550 (bottom).

Figure 9 shows the appearance of the test surfaces covered with the PEG containing SABC. These are representative of the surfaces used in the study. While the samples were subject to hard fouling, regions of the panels showed positive performance. Those polymers with longer PEG brushes appeared to have slightly better performance. Surfaces coated with semifluorinated groups showed similar positive though non-uniform behavior.

DISCUSSION

As part of the program, large plaques were coated with surface-active block copolymers on SEBS thermoplastic elastomer base layers. Samples required the development of new larger scale polymer syntheses of semifluorinated and PEG-modified SABCs to enable large scale coating. A new spray coating method was also developed to enable the deposition of these new coatings. Analysis of the plaques included pseudobarnacle testing and ocean immersion studies. In addition the films were reproduced on a smaller scale for testing with *Enteromorpha* zoospores. Surface analysis including NEXAFS studies, AFM and contact angle measurements all were used to characterize the perfection of the SABC surface for correlation with marine testing.

Most literature reports on contact angle measurements are concerned with water drop (static or dynamic) contact angle. While this is an important measurement for many experiments, it may be of less use in systems that are immersed in water for extended periods. Since marine organisms interact with wet surfaces, the captive bubble technique is a more relevant measure of the surface energy in the context of marine fouling. Captive bubble contact angle values are more akin to receding contact angles of water drops, than they are to advancing angles. Thus, it is consistent that the 90° captive bubble contact angle of the fluorinated surface of PS/PI(25/15)Br-H6F8 surface is close to the 95° receding contact angle for water, typical of PTFE. While it is evident that PS/PI(25/15)OH-PEG550 is more hydrophobic than the PS/PI(25/15)OH-PEG164 surface, it would have been expected that the contact angles would be similar. Kinetics of hydration and reconstruction may play a significant role here.

The settlement of *Enteromorpha* zoospores was lower on all test surfaces, compared to glass and the SEBS base. There was only a small influence of the type of copolymer attached to the SEBS base even though the modifications resulted in surfaces of very different wettability. This result contrasts with previous data on spore settlement on mixed alkane thiolate self-assembled monolayers where it was shown that spore settlement increased 3-fold for an increase in water contact angle from 60° to 90°. However, measurements of adhesion strength of the settled zoospores showed substantial differences between the copolymers, with a positive correlation between levels of removal of attached spores and low surface wettability.

Surfaces characterized by contact angle measurements, and analogous bilayers on microcope slides were tested by both NEXAFS and AFM. NEXAFS results indicate good orientation of the SF side groups. While contact angle measurements and NEXAFS studies indicated that the desired surfaces had been produced, ambiguous or poor fouling results lead to further studies. AFM studies of the SF surfaces indicate a patchy coating consisting of fluorinated liquid crystalline domains. This was observed with both, the bilayers, and the blend films. For the coatings with PEG side group, contact angles are consistent with a high degree of PEG at the surface. The patchiness of the surfaces depends on how the coatings were applied on the substrate. Previous studies have shown that the patchiness varies with processing conditions, viz. the solvent used for spin coating, the concentration of the SABC solution used for spin coating, etc. The non-uniformity of the coated surface could also be the cause of the observed molecular-weight effects on fouling release, as rheological properties of the coating solution change with molecular-weight.

Initially, for the pseudobarnacle tests, panels coated with SABCs prepared from high molecular-weight PS/PI block copolymers (viz., 25,000 g/mol and 15,000 g/mol PS and PI blocks) were used. Although the results with the SF side group polymers showed some promise, they were not optimal because the pull-off force was relatively high. Lower molecular-weight SABC polymers were then prepared and tested. However, the release performance declined even further – the pull-off force exceeded the range of the force gauge at 20 pounds. It is unclear why these coatings showed a poor performance in spite of the fact that the coating method was modified to produce a more uniform film of SABC on the SEBS – the initial panels tested had shown a non-uniform coating across the surface (cf. **Figure 3**). It should be noted that the PEG containing materials are expected to perform well only when immersed in water, and while the pseudobarnacle tests are performed in the dry state, thereby giving force gauge measurement at the maximum of 20 pounds. These results merit two comments. The pseudo-barnacle tests showed that the overall coating process was not satisfactory. At the same time, it is not clear if the test is appropriate for these coatings. The solvent like state of the uncured epoxy is suspected of destroying the SABC surface.

TRANSITION PLAN

1. Optimize molecular factors that affect coating performance:
   - The surface-active side groups were attached to the polymer backbone via ether linkages. The chemistry of forming an ether linkage gives less than complete functionalization of the polyisoprene backbone. The residual bromine groups on the PI block will have a detrimental effect on the fouling release properties. Attachment of the side groups by an ester linkage is instead more facile, giving almost complete functionalization. However, ester linkages are prone to hydrolysis upon prolonged exposure to water. Thus, methods to improve the extent and method of attachment of the side groups to the polymer backbone will be required.
   - The effect of molecular weight and relative composition of the starting PS/PI block copolymer on coating application and processing, will be investigated on a laboratory scale.
   - The effect of the side groups on the coating performance will be studied: the relative numbers of CH_2 and CF_2 groups on each SF side-chain, and the molecular-weight of PEG will be varied, and their effects on the fouling release behavior will be investigated.

2. Analyze large scale production possibilities, and the cost of material synthesis and coating systems.

3. Improve spray coating process to enable creation of uniform, patch free surface.

4. Perform small scale marine panel testing.

CONCLUSION

The main project accomplishments are listed below:

- Synthetic design and scale-up of surface-active block copolymers were successfully completed.
- A new spray coating method for SABC deposition was developed.
- Large test structures were prepared, and shipped to Carderock, where pseudobarnacle testing and marine evaluation took place.
- A successful analysis of the issues associated with coating methods was completed.
- New strategies were developed for improved coating preparation, and are in the early stages of implementation.

It is clear from the surface characterization, as well as pseudobarnacle adhesion testing, that further process improvements (synthesis and processing) are necessary before these coatings become suitable for commercial application. However, the results show that through proper molecular design of these bilayer coatings, a reduction in the pseudobarnacle adhesion force is possible. The semifluorinated bilayer coatings may be an economically feasible direction toward environmentally friendly marine fouling resistance/release coatings.

RECOMMENDATIONS

It is planned that further investigations into the structure-property relationship of the surface-active block copolymers will be carried out on a laboratory scale using well-controlled experiments and known organisms. Factors such as SABC molecular-weight, block ratio, and coating thickness should be optimized before significant steps towards commercial application be undertaken. New materials that can reduce biofilm formation by marine bacteria, or make use of low-energy buoy groups to bring hydrophilic groups to the surface, are under consideration. Panel tests should follow successful laboratory-scale testing of these coatings for fouling release properties.

LIST OF PUBLICATIONS

Peer-reviewed papers

"Coatings Based on Side-chain Ether-linked Poly(ethylene glycol) and Fluorocarbon Polymers for the Control of Marine Biofouling", Youngblood, J.P.; Andruzzi, L.; Ober, C.K; Hexemer, A.; Kramer, E.J.; Callow, J.A.; Finlay, J.A.; Callow, M.E, *Biofouling* **2003**, *19*, 91.

Conference proceedings

"New materials for marine biofouling resistance and release: Semi-fluorinated and PEGylated block copolymer bilayer coatings", Jeffrey P. Youngblood, Luisa Andruzzi, Wageesha Senaratne, Christopher K. Ober, Jim A. Callow, John A. Finlay, and Maureen E. Callow, *Polymeric Materials: Science & Engineering* **2003,** *88,* 608.

"Block Copolymers as Surface Modifiers: Synthesis, Characterization and Relevance to Fouling Release and Biostability" Christopher K. Ober, Jeffrey P. Youngblood, Luisa Andruzzi, Wageesha Senaratne, Xuefa Li, Alexander Hexemer, and Edward J. Kramer, *Polymeric Materials: Science & Engineering* **2003,** *88,* 612.