

PP756-2



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3900
Ser D361/01-99
23 Feb 99

From: Commanding Officer, Space and Naval Warfare Systems Center, San Diego
To: Executive Director, Strategic Environmental Research and Development Program
(SERDP), Arlington, VA

Subj: FINAL REPORT

Ref: (a) Sponsor reporting requirements as published on the SERDP website
(www.serdp.gov)
(b) EMAILCON SPAWARSYSCEN SAN DIEGO (D361) M. Putnam & R.
George/Office of Naval Research (331) K. Wynne of 7 Jan 99

Encl: (1) Final Report entitled "Fluorinated Ship-Hull Coatings for Non-Polluting Fouling
Control", SERDP Project PP/756/456.

1. Per references (a) and (b), enclosure (1) is forwarded for Space and Naval Warfare Systems Center (SPAWARSYSCEN) input into the final report for the Strategic Environmental Research and Development (SERDP) project PP/756/456, coordinated with the Naval Research Laboratory, Washington, D.C. This report describes work completed before funding for the SPAWARSYSCEN effort was abruptly stopped prior to its completion.

2. Please direct technical questions concerning this report to Dr. Robert George, commercial (619) 553-2776, DSN 553-2776, fax (619) 553-6305, or email george@spawar.navy.mil.

R. H. Moore

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By direction



FINAL REPORT (SERDP PROJECT PP/756/456)

FLUORINATED SHIP-HULL COATINGS FOR NON-POLLUTING FOULING CONTROL

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OBJECTIVE

The goal of this project is the development of non-polluting, easy fouling-release hull coatings based on flexible, low surface energy polymers. Currently, conventional antifouling coatings contain copper as a toxicant. The copper leaching from these coatings represents an environmental hazard and is subject to increasing regulations that may impact normal fleet operations. In contrast, coatings with minimally adhesive surfaces do not introduce toxic materials into the environment, but work by the non-stick nature of the polymer surface rather than toxicity of a released antifouling agent. This research seeks to quantitatively define the deficiencies of non-toxic minimally adhesive coating systems in terms of fundamental parameters so that systematic improvements can be made toward the "ultimate" fouling release surface.

BACKGROUND

Protection of ship-hulls from marine fouling organisms is essential for efficient fleet operation and energy conservation. Historically, to achieve this protection, ship hulls have been coated with materials that contain toxic materials such as tar and pitch, arsenic, inorganic heavy-metal compounds, and metallo-organics including organo-arsenic, organo-mercury, and organotin compounds. The present Navy standard uses copper-based paints for this purpose resulting in the potential for an environmental hazard due to continuous release of copper as the active antifouling agent. A cruiser-size ship (35,000 ft² hull area) releases approximately two pounds of copper per day that potentially brings approximately five million gallons of sea water to toxic copper concentrations. Dozens of ships painted with conventional toxic antifouling paints can make a significant environmental impact in an enclosed harbor.

Since the Navy operates both in U.S. and foreign waters, compliance with Federal, State, local, and host country environmental regulations is required to ensure unconstrained operation. To meet its needs, the Navy has had a strong commitment to develop and maintain an environmentally sound ship for the 21st century. The work described herein contributes toward this effort with the goal of developing a toxin-free coating that resists the attachment of marine fouling organisms by taking advantage of the weak adhesion characteristics of materials that have low surface free energies. The specific Navy requirements addressed by this work include 3.1.8.h: "Prevention of hazardous discharge from ship in-water hull cleaning" and 3.1.4.b: "Non-hazardous Antifouling/Fouling Release Hull Coatings"; priority 'H' under the Compliance Pillar.

All marine fouling organisms use biopolymeric adhesive secretions for attachment. The strength of adhesion, expressed as the thermodynamic work of adhesion (W_A), is the work required to separate the adhered liquid from the solid surface, or the sum of the surface free energy of the solid (γ_s) and the pure liquid surface tension (γ_l) minus the interfacial tension (γ_{sl}), as originally proposed by Dupre' in 1869.[1]

$$W_A = \gamma_s + \gamma_l - \gamma_{sl}$$

Equation { 1 }

From this equation, it is clear that the lower the surface free energy of the solid (γ_s), the weaker the adhesion. Hull coatings with sufficiently low surface energy should prevent fouling because organisms should not be able to adhere to it. Further adaptations based on this theory have made possible the experimental determination of low surface energy properties, such as contact angles and wettability of solid surfaces.[2,3]

The lowest surface free energies can be created by adsorbed monolayers of closely packed perfluorinated compounds.[4] Since adsorbed monolayers are not practical as hull coatings, the present work has simulated such systems by binding perfluorinated compounds onto a polymeric backbone to create polymers with perfluoroalkyl sidechains. These types of polymeric materials were previously shown to exhibit some of the lowest surface free energies, far lower than that of Teflon™, in addition to promising properties for biofouling control. [4-7]

TECHNICAL APPROACH

The specific technical objective of this project is the development of nontoxic, zero discharge coatings that protect ship-hulls from marine fouling organisms. Unlike conventional antifouling paints, such coatings do not contain toxic materials, rather they are designed to resist fouling by allowing only weak adhesion of fouling organisms. In order to minimize bioadhesion, materials with the lowest possible surface free energy must be utilized and evaluated. The planned approach in this work has been to: (1) Simulate adsorbed fluorinated monolayers by synthesizing comb-type polymers with perfluorinated side-chains for maximum effectiveness; (2) Determine the minimum amount of perfluorinated monomer needed for optimum performance; (3) Reduce the amount of the expensive perfluorinated moiety by copolymerization or block-polymerization with non-fluorinated monomers to reduce cost; and (4) Verify the effectiveness of the perfluorinated polymeric materials against the adhesion of marine fouling organisms.

RESULTS AND ACCOMPLISHMENTS

This effort has focussed on the synthesis and characterization of a series of model polymeric materials, the subsequent preparation and characterization of coatings (multiple types) using each distinct polymer product, and the quantitative evaluation of each coating under laboratory and field conditions to evaluate bio-fouling release performance as a function of the systematically varied chemico-physical properties of both polymer and coating. This performance is then used to systematically optimize properties of the polymer and the coating for maximum effectiveness. Each stage of this process relies upon the others for feedback into repeat cycles of the optimization scheme. For purposes of statistical significance during quantification of bio-fouling performance, a large number of replicate coating samples and analyses are required. In addition, reproducibility, both in evaluation methodology and sample preparation, requires that replicate samples of each coating be prepared from the same or identical polymer batch, and each of these requires replicate laboratory and field analyses. The logistics of such an approach translates into an intensive program, which is further complicated by the bio-fouling season during coating evaluation. As a result, in-field testing of coatings was ideally performed during the height of each annual fouling season with a maximum number of replicates for each distinct type of polymer and coating. When taken together, these data can be used to derive fundamental dependencies of bio-fouling organism attachment on systematically varied polymer and coating properties.

It is also important to note that the funding for this project was abruptly stopped 1-1.5 years prior to its scheduled completion. This profoundly affected the project goals and the technical approach described above, most significantly influencing any coatings preparation, evaluation, and optimization being performed at the time, and as a result, these efforts were not continued. Only those materials which were furthest along were prepared and evaluated in the field, specifically, the polymer series prepared from methyl-acrylate (MA) and perfluorooctyl-acrylate (PFOA) monomers. Other polymer series, though synthesized on small scales during the earlier

phases of the project, were not utilized for coating preparation and subsequent field evaluation (*i.e.* they were not scaled up to levels suitable for coatings work due to funding constraints). The synthesis and characterization phase of the project was completed and a manuscript is now being prepared which more fully describes these efforts, and in particular, NMR characterization of the PFOA/MA polymer series.[8] The results and experimental details of coating studies using only the PFOA/MA series as model polymers are found in Appendix A. Other results and experimental details which were reported as the project progressed are also included in Appendix A.[9-12] A future manuscript is planned describing coating preparation, in-field testing, and structure-property-performance characteristics of the polymer coatings investigated in this work. The results of all work related to this project will be transitioned to coatings formulators in the Navy and private sector for use in optimizing fouling-release coatings for use in marine fouling environments. A brief narrative is included below for each experimental aspect of this program.

Materials Synthesis. In efforts previous to this work, a low surface free energy approach was explored for several chemical systems, all of which incorporated fluorine-containing materials into a polymeric matrix, resulting in low surface free energies. A number of useful systems were successfully demonstrated in our laboratory by addition of perfluorinated surfactants to polymers or by preparation of comb-like polymers with siloxane, polyacrylate, and polymethacrylate backbones with perfluorinated long sidechains.[4-7] The use of additives resulted in low surface free energy materials, but this approach was abandoned because of susceptibility to molecular rearrangement upon exposure to water, leading to a surface free energy increase. Although costly and difficult to process, perfluorinated siloxanes exhibited excellent performance and properties. Homopolymers prepared from perfluorinated acrylate and methacrylate monomers exhibited low surface free energies, but with undesirable physical properties and high cost. However, perfluorinated copolymers prepared from these monomers, showed much lower than expected surface free energies and much-improved physical properties, in addition to being economically feasible. These polymeric materials were chosen as a model polymer system to form a basis for understanding and developing formulations and methodologies necessary to evaluate and optimize coatings for maximal resistance to bio-fouling adhesion. Acrylate polymers have a number of beneficial properties which make them amenable as model systems including

straightforward and easily controlled polymerization chemistry, high strength and durability, low permeability to oxygen and water, and as indicated above, low surface energies. The details of our synthetic work are described in Appendix A. Because consistency and reproducibility are critical when comparing properties and performance, the reaction chemistry was controlled using process automation in nearly all cases. The final automation of these synthetic processes consisted of three side-by-side chemical reactors with computerized control and measurement of critical parameters such as temperature and reactant addition rate. Two of the three synthetic reactors are shown assembled in Figure 1. For each distinct target polymer, multiple (replicate) syntheses were performed. This generally consisted of an initial small scale synthesis, subsequently followed by designed increases in synthetic scale.

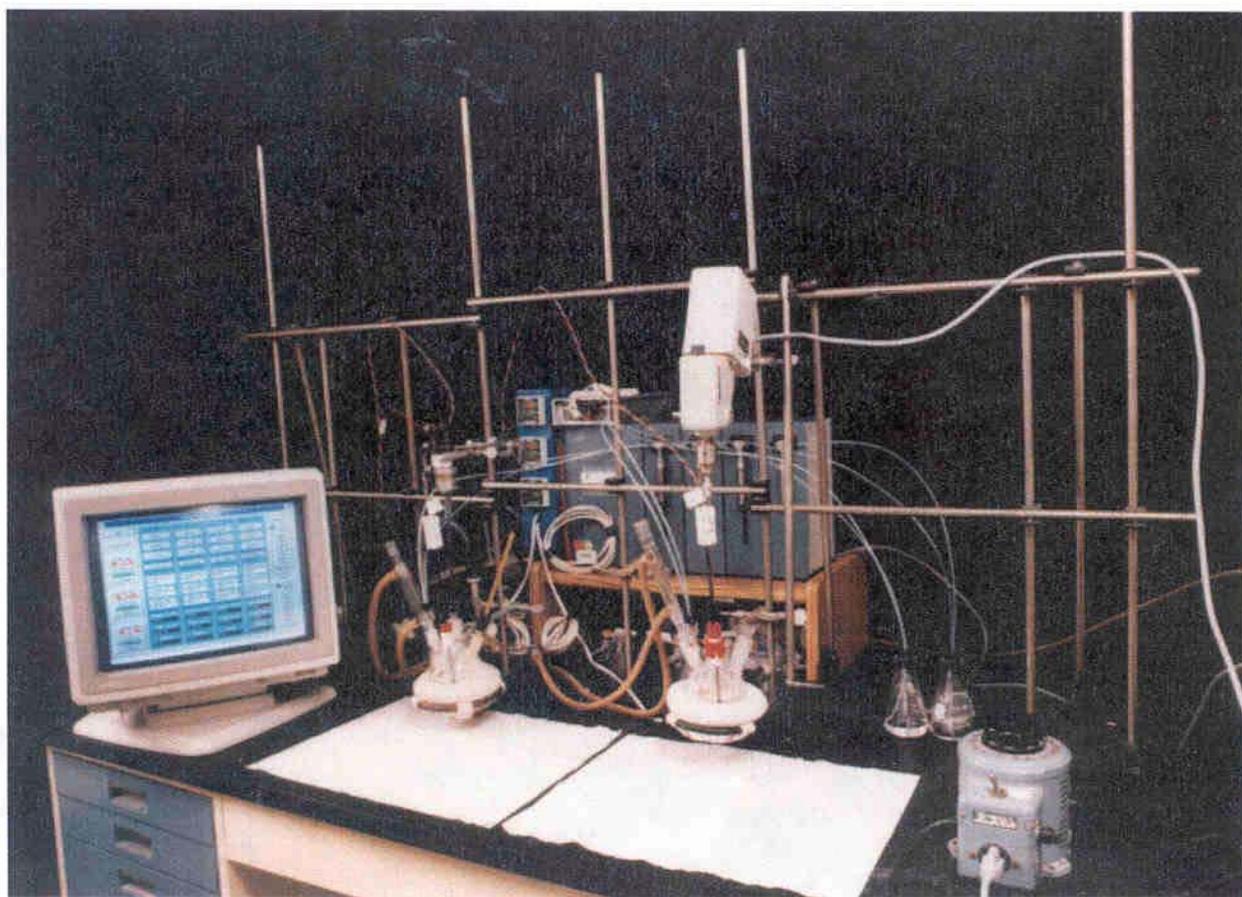


Figure 1. Computer-controlled synthetic reactors used in this study. The third reactor assembly is not pictured here.

The above synthetic effort resulted in a large matrix of distinct polymeric materials, each with systematically designed variations in structure and properties, and synthetically replicated to verify product and property reproducibility. This portion of the program was labor intensive but resulted in four polymer series, two with acrylate backbones and two with methacrylate backbones, both having perfluoroalkyl sidechains prepared with systematic variations in molecular structure (random and segmented copolymers), composition (fluorine content), and resultant physical characteristics (*e.g.* thermal properties, molecular weight, color and transparency, flow behavior, and toughness/flexibility).

Materials Characterization and Properties. Reaction analytics, when necessary, were performed using gas chromatography and/or infrared spectroscopy. Each synthetic product was isolated and purified as described in Appendix A. The molecular weight distributions of purified products were determined with gel permeation chromatography using polystyrene polymers as primary molecular weight standards. Molecular composition was determined using conventional elemental carbon, hydrogen, and fluorine analyses. Multiple analyses were performed to confirm these elemental compositions. In general, random copolymer syntheses resulted in elemental compositions much closer to the target (nominal) compositions, simply because these syntheses were performed under more rigorously controlled reaction conditions. Thermal analyses of the polymers were performed as described in Appendix A and generally resulted in melting point and glass temperature variations predicted by copolymer models with intimate mixing of the two monomer units and with systematically varied stoichiometries. Molecular structure characterization of the polymers products included infrared (IR) spectroscopy and both solution and solid state (MAS) nuclear magnetic resonance (NMR) spectrometry. Prior to preparation of coatings, polymer solution viscosity properties were evaluated and optimized for application using conventional spray-coating technologies.

Coating Preparation and Characterization. In the initial stages of preparing coatings from new polymer materials, films were applied to appropriately treated flat panel surfaces by casting the polymers from solution. These crude coatings were useful for preliminary measurements of contact angles to initially calculate surface energies, and for characterizing the inherent morphologies and structural characteristics of the polymers as formed from solution. The most critical parameter for controlling the surface morphology and structure is the viscosity of the solution from which the coating is formed. This is related to the mobility of molecules in the solution; at higher concentrations, crystallization is inhibited and molecular mobility is decreased. As a result, the molecules tend to lock into a more liquid-like or glassy arrangement upon solvent evaporation. A lower concentration tends to allow crystallization to occur and reduces the ability of the solution to form a glassy solid upon solvent evaporation. Polymers were sprayed onto substrates to ultimately provide a large number of coating samples prepared under nearly identical conditions for each distinct polymer. This led to minimal reproducibility and consistency problems related to morphological and structural variation from sample to sample. By varying the viscosity of the polymer solution, control over morphology and structure of the coating surface was achieved so that the effects of such coating properties on performance could also be evaluated in the field testing phase. Automation of the sprayer itself was instrumental in removing human inconsistencies from coating preparation procedures which can be detrimental to the comparison of coating performance results. The automated spraying apparatus is shown in Figure 2 and technical details can be found in Appendix A.

The process for optimizing the sprayer consists of first spraying flat panels for initial evaluation of their properties (morphology, coverage, surface energies, etc.), optimization of the spraying parameters to give the required properties (by reapplication using optimal parameters and checking properties again), and then utilizing these parameters as a starting point for spraying other substrates. This minimizes the optimization time required for new substrate geometries. In the case of fouling evaluation, substrates consisted of fiberglass rods (0.25" diameter x 4" long). Sprayer optimization and representative properties (morphologies, coverage, surface energies, etc.) for coatings prepared from our polymers are described in Appendix A. Polarized surface infrared spectroscopic measurements on thin polymer films cast from solution indicated no

preferred orientation of perfluorinated sidechains in the films, even though differences in morphology were noted as a function of type of polymer and method of preparation.

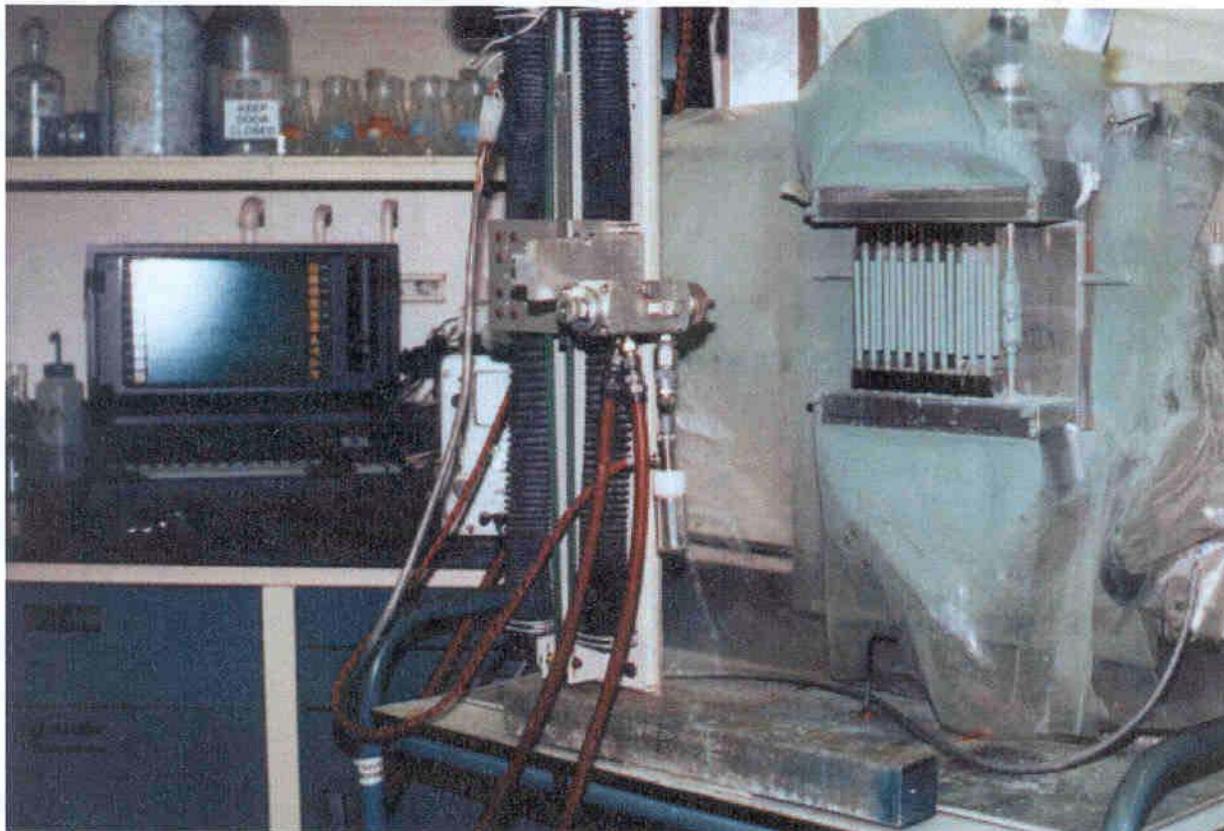


Figure 2. Computer controlled HVLP sprayer for coating various substrates. Assembly is shown for coating 18 fiberglass rods at one time. The rods are rotated at controlled speeds and the spray head and rods are translated as necessary on x, y, z translation axes to provide a uniform coat.

Coating Performance Evaluation. Evaluation of coatings was performed both in the laboratory and in the field (see Appendix A). Laboratory studies consisted of simulated barnacle adhesion measurements using a standardized two-part epoxy "pseudo-barnacle" attached to the surface of flat coatings. These measurements provided a means of comparing relative adhesion properties of the low energy surfaces, but were of only limited value due to a lack of significant variation in surface energies for the polymeric materials in this study. However, in cases where surface

energies were significantly different, a corresponding dependence was generally reflected in these adhesion measurements. Studies were also undertaken to determine the force required to remove individual mussel byssus threads, previously attached by mussels in a laboratory aquarium. These measurements were of limited value for rapid screening purposes, but provided some insight into mussel settling habits. The organisms would typically not settle on the surface of our polymers, as they are undesirable surfaces compared with other, higher energy surfaces found in the aquarium environment. When they did settle, great variability in the bioadhesion of single byssus threads to the surface was noted. Evaluating an adequate means of pulling a single byssus thread off in a reproducible manner was also found to be troublesome.

Performance evaluation of the coatings was initially performed in Pearl Harbor by the University of Hawaii, through coordination with the Office of Naval Research Biofouling Program, to determine appropriate methodologies for biofouling evaluation. It soon became necessary to evaluate a much larger number of replicates on a regular basis and perform other measurements on the exposed sample coatings, so the biofouling evaluation was then performed solely at our facility in San Diego Bay. Preliminary biofouling release performance measurements at Pearl Harbor served as a baseline for the evaluation methodology. Biofouling evaluation of the fouling-release coatings in this study comprises exposure for 28 days, with daily observation and monitoring of biofouling progress. At 28 days, the coverage (biomass and area) of organisms on the surface is evaluated. The measurement of wet weight biomass was of limited value due to the large variation in organism water content, but this problem was somewhat avoided if dry weight biomass was measured. This had the drawback of being very time-consuming and was not performed in all cases. For this reason, biofouling evaluation by coverage area is the focus of this work and is most conveniently approached (logistically simplified) by evaluating the coverage of organisms broadly at the species level, which crudely approximates the biofouling by mechanism of attachment. The following organisms from the Kingdom Animalia were evaluated primarily at the Phylum or Subphylum level: Tunicata (solitary and colonial), Bryozoa, Cnidaria (Anthozoa and Hydrozoa), Arthropoda (primarily *Balanus*), Porifera, Annelida, Mollusca (primarily *Mytilus*), and "other" hard or soft foulers. Fouling organisms identified from the Kingdom Plantae were specified only as Algae. All coatings were evaluated using these categories, but

only data for fouling organisms present concurrently on all of the coatings (co-foulers) were used for performance comparisons between coatings. Additionally, it is well known that a biofilm is usually present during the first 1-2 weeks of exposure, although, initial bio-film formation is important to many, but not all forms of macrofouling. Because it is not within the scope of this project, biofilms were not evaluated or quantified in this study. Underwater videography was useful for observing different stages of biofouling and succession of different organisms on the surface of the coatings over the 28 day exposure cycle. Though not performed routinely or useful quantitatively, this method was occasionally used to observe underwater cleaning of coatings which performed well in laboratory cleaning studies. Cleaning was quantified by evaluating the biofouling coverage of each exposed sample both before and after standardized waterjet cleaning measurements described in Appendix A. These measurements provide a means to quantitatively compare the cleaning behavior of different coatings on the basis of the fouling coverage which remains after cleaning. Obviously, the more fouling removed in this process, the better the coating efficacy. Cleaning studies for polymer coatings are detailed in Appendix A. Representative trends in coating cleaning efficiencies are illustrated in Tables 1 and 2 as a function of selected polymer and coating properties for the PFOA/MA model coatings investigated in this work.

Polymer	Cleaning Efficiency as a function of:			
	Surface Roughness		Viscosity	
	trend	r	trend	r
75/25 PFOA/MA-R	(-)	0.96	(+)	0.97
50/50 PFOA/MA-R	(-)	0.88	(+)	1.00
25/75 PFOA/MA-R	(-)	0.67	(+)	0.81
HP	(-)	0.99	(+)	0.79
75/25 PFOA/MA-S	(-)	0.06	(-)	0.93
50/50 PFOA/MA-S	(+)	0.97	(-)	0.98
25/75 PFOA/MA-S	(-)	1.00	(-)	0.84

Table 1. Cleaning efficiencies for PFOA/MA copolymers as a function of coating surface roughness and spray viscosity. (+) or (-) indicates a cleaning efficiency increase or decrease,

respectively, as the surface roughness or spray viscosity is increased, and "r" is the Pearson correlation.

Coating	Cleaning Efficiency as a function of:			
	Fluorine Content		Melting Point	
	trend	r	trend	r
30-R	(+)	0.98	(+)	0.97
80-R	(+)	0.81	(+)	0.77
130-R	(+)	0.77	(+)	0.24
30/80/130-R	(+)	0.52	(+)	0.29
30-S	(+)	0.75	(+)	0.80
80-S	(+)	0.87	(+)	0.27
130-S	(+)	0.87	(+)	0.48
30/80/130-S	(+)	0.36	(+)	0.15

Table 2. Cleaning efficiencies for PFOA/MA copolymer coatings as a function of fluorine content and polymer melting point (if measurable). (+) or (-) indicates a cleaning efficiency increase or decrease, respectively, as the fluorine content or melting point is increased, and "r" is the Pearson correlation.

CONCLUSIONS AND RECOMMENDATIONS

It has been confirmed in this work that low surface energy is a required property for a successful fouling release coating. For fluoropolymers, lower values appear to be better, although, it is apparent that coatings with an optimal low surface energy parameter are not independent of other physical properties. Thus, surface energy does not entirely dictate the level of performance. To better understand the effects of other properties, field evaluation of coatings as described in this effort must be performed with a larger number of replicates and with other polymers as originally proposed in order to provide a greater degree of statistical credibility. Because of funding cuts,

this was not possible in this work, as such an approach is both a time and labor intensive process. As a result, the significance of the field data presented here must be considered preliminary in nature. Despite this difficulty, the work described here has demonstrated and provided the methodology whereby coatings development directed at biofouling release can be optimized to provide relatively fast optimization of physical and chemical properties of both the bulk material (fluoropolymer, in this case) and of the coating itself. Previous methods of coatings development in this area have traditionally relied on the testing of an individual hypothesis from a materials chemistry perspective with only a pass/fail approach for biofouling release performance. Without significant and quantitative statistical input from the biological perspective, optimizing the material or coating becomes much too tedious, forcing the coatings formulator or synthetic chemist to prepare a new coating or material without significant feedback into the original hypothesis. The underlying disadvantage in attempting to quantitatively use growth and removal of biofouling as an indicator for coating performance optimization is the great amount of variation in many biologically diverse fouling communities found in real world environments and the resulting requirement of collecting statistically significant fouling data. It is not as simple as measuring a chemical or physical property to see if that single property in the designed coating system has been optimized by means of a change in chemistry or methodology. In contrast, each biological organism can respond quite radically to subtle differences in coating properties. This response must be taken into consideration during any coating optimization process, requiring that a large amount of effort be directed at repetitive field testing of enough replicates to provide statistical significance. A comprehensive approach, such as described in this work, should be adopted to enable coatings formulators to optimize new synthetic materials and new types of coatings for biofouling control on ship hulls and/or other structures in marine environments.

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10. "Synthesis of Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers", E. M. Arias, M. D. Putnam, P. A. Boss, R. D. Boss, A. A. Anderson, and R. D. George, *Polymer Preprints*, **38**(1) (1997) 512.
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12. "Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers: 2. Coating Preparation, Characterization, and Properties", E. M. Arias, J. L. Gray, L. B. Truong, A. A. Anderson, M. D. Putnam, R. D. Boss, and R. D. George, *Proceedings of the First U.S./Pacific Rim Workshop on Emerging Non-Metallic Materials for the Marine Environment* (1997) 4.28.

TECHNICAL/CONFERENCE PRESENTATIONS (ABSTRACTED)

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"Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers: 1. Synthesis and Characterization", 1st U.S./Pacific Rim Workshop on Emerging Non-Metallic Materials for the Marine Environment, Honolulu, HA, 1997.

"Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers: 2. Coating Preparation, Characterization, and Properties", 1st U.S./Pacific Rim Workshop on Emerging Non-Metallic Materials for the Marine Environment, Honolulu, HA, 1997.

"Synthesis of Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers", 213th American Chemical Society National Meeting, San Francisco, CA, 1997.

"Solid State ¹³C-NMR Investigations of Perfluorooctylacrylate-Methylacrylate Copolymer Blends", San Francisco, CA, 1997.

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"Cleaning Behavior and Optimization of Low Surface Energy Coatings", Office of Naval Research Fouling Release Coatings Review, Bethesda, MD, 1998.

TECHNICAL REPORTS/PUBLICATIONS/PROCEEDINGS (ATTACHED AS APPENDIX A)

“Solid State ^{13}C -NMR Investigations of Perfluorooctylacrylate - Methylacrylate Copolymer Blends”, K. L. Altmann, L. H. Merwin, and R. D. George, *Polymer Preprints*, **38(1)** (1997) 786.

“Synthesis of Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers”, E. M. Arias, M. D. Putnam, P. A. Boss, R. D. Boss, A. A. Anderson, and R. D. George, *Polymer Preprints*, **38(1)** (1997) 512.

“Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers: 1. Synthesis and Characterization”, E. M. Arias, M. D. Putnam, P. A. Boss, R. D. Boss, A. A. Anderson, and R. D. George; *Proceedings of the First U.S./Pacific Rim Workshop on Emerging Non-Metallic Materials for the Marine Environment* (1997) 4.17.

“Perfluorinated Acrylate and Methacrylate Fouling-Release Polymers: 2. Coating Preparation, Characterization, and Properties”, E. M. Arias, J. L. Gray, L. B. Truong, A. A. Anderson, M. D. Putnam, R. D. Boss, and R. D. George, *Proceedings of the First. U.S./Pacific Rim Workshop on Emerging Non-Metallic Materials for the Marine Environment* (1997) 4.28.

APPENDIX A

Solid State ^{13}C NMR Investigations of Perfluorooctyl Acrylate/Methyl Acrylate Copolymer Blends

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Introduction

Coatings used to protect ship hulls from marine fouling organisms are essential for efficient and economic Fleet performance. Current antibiofouling strategies utilize copper-containing compounds as toxic agents that poison the organisms. These materials are highly regulated and pose significant environmental hazards. The present effort uses a different mechanism for fouling control, in which the physical properties of the surface are utilized to allow easy release (and removal) of the organisms.¹ Since these low surface-free-energy coatings do not release any toxic materials, the environmental impact should be greatly reduced. A series of environmentally-friendly fluorinated polymer blends are under investigation as candidate replacements for copper-containing coatings.

In order to optimize the characteristics of the candidate polymer blends and to correlate surface properties with antibiofouling behavior, it is important to characterize these novel materials at the molecular level. Solid state ^{13}C NMR spectroscopy provides a means of analyzing these blends for features such as structure, crystallinity, and phase morphology. In the work reported herein, solid state NMR methods have been utilized to investigate the molecular-level miscibility of the two components in a series of varying copolymer blends of perfluorooctyl acrylate (PFOA) and methyl acrylate (MA).

Experimental

The following PFOA/MA copolymer blends were synthesized: PFOA homopolymer, 75/25 PFOA/MA, 50/50 PFOA/MA, 25/75 PFOA/MA, and MA homopolymer. The blends were synthesized according to a single-addition scheme, in which all of the least reactive monomer (1H,1H-perfluorooctyl acrylate) is placed in the reaction vessel and the most reactive monomer (methyl acrylate) is added incrementally with the initiator, 2,2'-azobis-(2-methylpropanitrile). Details regarding the syntheses can be found in a companion paper in *this Journal*.²

Solid state NMR experiments were performed on a Bruker MSL-200 NMR spectrometer operating at 50.323 MHz for ^{13}C and 200.13 MHz for ^1H . A 7mm DB/MAS probe was employed. Due to the nature of the samples, powdering was not possible, and it was necessary to use inserts (made of Kel-F®) to effect spinning.³ Typical spinning speeds were 4.4 kHz. The ^1H and ^{13}C 90° pulse lengths were 5 μs . A ^1H decoupling field strength of 50 kHz was used. Typical relaxation delays were 5 s. The ^1H rotating-frame relaxation time ($T_{1\rho}^{\text{H}}$) was measured by spin-locking the ^1H magnetization prior to cross polarization to the ^{13}C nuclei. A spin-locking field of 50 kHz was used and contact times ranged from 250 μs to 10 ms. All spectra are referenced to TMS using adamantane as a secondary reference.

Results and Discussion

In Figure 1 are shown the ^{13}C CP/MAS NMR spectra of the PFOA homopolymer, the PMA homopolymer, and three intermediate copolymer blends of the two components. The peaks can be assigned as follows: the peak at about 40 ppm is an overlap of PFOA and MA main-chain carbons. The sharp resonance at 52 ppm is from the methoxy carbon of MA. The peak at about 59 ppm arises from the CH_2 's in the PFOA side chain. The broad feature at about 120 ppm is due to CF_2 's in the PFOA side chain. Finally, the peak at 175 ppm is an overlap of PFOA and MA carbonyl carbons.

Shown in Figure 2 is a typical set of $T_{1\rho}^{\text{H}}$ relaxation data. The sample used was a copolymer blend of 50/50 PFOA/MA. The relaxation behaviors of four of the resonances were followed, as indicated in the legend. The peak at about 120 ppm is too broad to allow analysis. Also included in this plot are the lines of best fit and the

corresponding $T_{1\rho}^{\text{H}}$'s for each line. From these data, it is clear that all of the peaks relax at essentially the same rate. The slopes agree within 6% of the average. This similarity in relaxation times results from rapid spin diffusion, which averages the relaxation times of the various components. Such data indicate that the components in this sample are homogeneously mixed to a distance of approximately 20 Å.⁴ If this mixing were not present, the individual resonances would tend to relax at rates similar to those of the corresponding homopolymer.⁵

The $T_{1\rho}^{\text{H}}$ results for the two homopolymers and the three blends are reported in Table 1. The $T_{1\rho}^{\text{H}}$'s are reported for the peak at 175 ppm (the carbonyl peak), the peak at 59 ppm (from PFOA only), and the peak at 52 ppm (from MA only). Also included in the table is the average $T_{1\rho}^{\text{H}}$, calculated from the relaxation curves of all the peaks, along with the scatter in the $T_{1\rho}^{\text{H}}$'s of each blend. The scatter gives an indication of how similar the slopes are for each sample. They are seen to deviate by at most 12%, and the error is generally much less. Since some of the resonances are broad and present at a level of only 25%, it is easy to understand how this error is introduced. It is expected that the carbonyl data are the most reliable, since the carbonyl peak is narrower and more intense than all other peaks in the spectra except for the methoxy peak in the spectrum of the MA homopolymer.

Shown in Figure 3 is a plot of the $T_{1\rho}^{\text{H}}$ curves for the five samples studied, using data from the carbonyl peak at 175 ppm. Also included are the lines of best fit. From this plot, it is clear that the various copolymer blends exhibit $T_{1\rho}^{\text{H}}$ values that are intermediate between those of the homopolymers. This is further evidence of intimate mixing of the two components. In addition, the trend of decreasing $T_{1\rho}^{\text{H}}$ as the percentage of MA is increased is very obvious and is supportive of the concept of a high degree of miscibility of the two components. It should be noted that, while the carbonyl peak is an overlap of two carbonyl resonances, all other resonances in the spectra, including the nonoverlapping resonances at 52 ppm and 59 ppm, display the same trends.

Conclusions

The technique of ^1H $T_{1\rho}^{\text{H}}$ measurement has been used to examine the miscibility of PFOA/MA copolymer blends. The homogeneity of these blends is evidenced in the agreement between $T_{1\rho}^{\text{H}}$'s within each blend and also in the trends that are observed in $T_{1\rho}^{\text{H}}$ values on going from PFOA homopolymer to MA homopolymer. Studies have shown⁶ that as little as 5 to 10% inhomogeneity leads to initial slopes (in the decaying part of the curve) that are closer to the homopolymer. There is no evidence of this type of decay in the data presented. Thus, it is clear that the two components are fully dispersed on a scale of approximately 20 Å.

Acknowledgments

This work is supported through the Strategic Environmental Research and Development Program. K.L.A. is supported by an ONR/ASEE postdoctoral fellowship.

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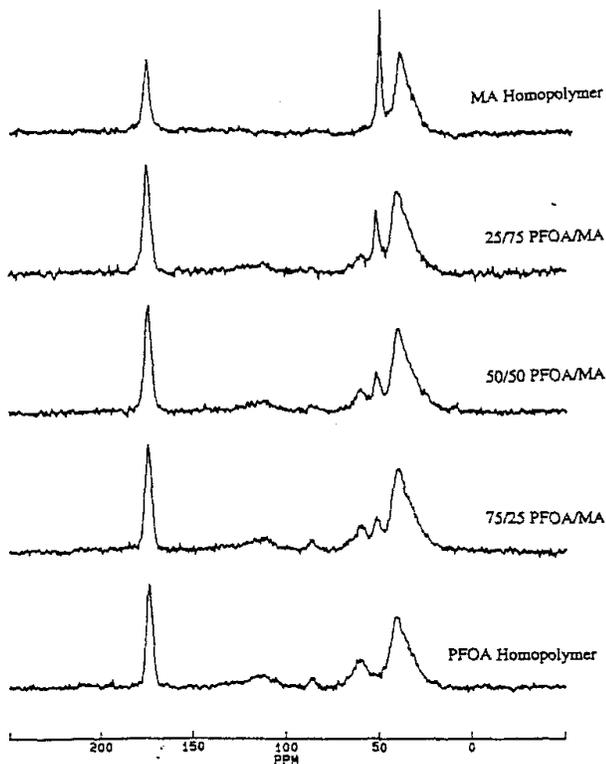


Figure 1. ^{13}C CP/MAS spectra of homopolymers and copolymers of PFOA and MA.

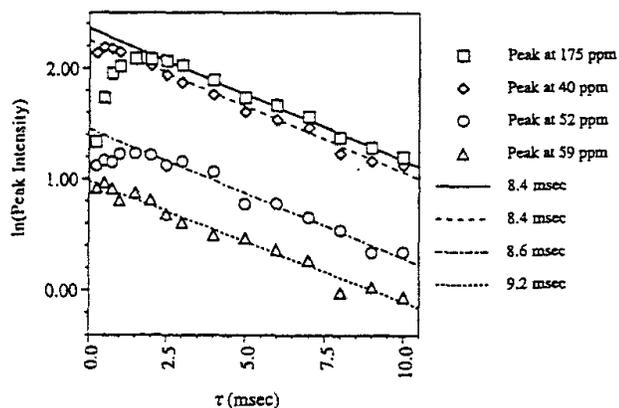


Figure 2. Decay of magnetization as a function of contact time for a 50/50 PFOA/MA copolymer blend. The four data sets represent four resonances, as shown in the legend. Also shown are the lines of best fit and the corresponding $T_{1\rho}^H$ values.

Table 1. $T_{1\rho}^H$ Values (in msec) of PFOA/MA Copolymer Blends

PFOA/MA	$T_{1\rho}^H$ (C=O) ^a	$T_{1\rho}^H$ (PFOA) ^b	$T_{1\rho}^H$ (MA) ^c	$T_{1\rho}^H$ (ave) ^d	Scatter (%) ^e
100/0	16.1	15.6	—	15.8	2
75/25	12.9	15.8	16.3	14.7	12
50/50	8.4	9.2	8.6	8.7	6
25/75	8.1	7.4	7.4	7.5	8
0/100	4.3	—	4.3	4.3	1

- a From peak at 175 ppm.
- b From peak at 59 ppm.
- c From peak at 52 ppm.
- d From all peaks.
- e Largest % error of any $T_{1\rho}^H$ value from $T_{1\rho}^H$ (ave).

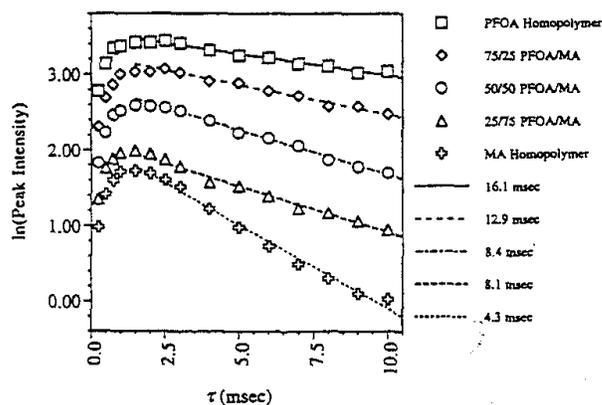


Figure 3. Decay of magnetization as a function of contact time for a series of PFOA/MA homopolymers and copolymer blends. Also shown are the lines of best fit and the corresponding $T_{1\rho}^H$ values.

SYNTHESIS OF PERFLUORINATED ACRYLATE AND METHACRYLATE FOULING-RELEASE POLYMERS

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INTRODUCTION

Straight-chain polymers with fluorinated sidegroups form a class of low surface-free-energy polymers which interact only weakly with polar liquids. Further, these materials are capable of withstanding harsh environmental conditions for extended periods of time. It has been shown that low surface free energy is a beneficial approach for materials which are to be used in marine fouling environments.¹ In such environments, marine fouling organisms produce bioadhesives which are secreted onto surfaces of substrata for purposes of initial attachment and subsequent fouling-organism colonization. Bioadhesion is a primary underlying mechanism which contributes directly to the problem of marine fouling. Previous and current solutions to this problem have predominantly included the use of anti-fouling coatings from which biocides are slowly released over time. This type of solution possesses an element of environmental risk and is the motivation for developing non-polluting, low-adhesion coatings, also referred to as fouling-release (FR) coatings, because fouling adheres only weakly and can be removed. Though it is apparent that low surface free energy is indeed a contributor to the mechanism of fouling-release, its exact role is still unclear, as is the role of other coating properties which are perhaps more critical than previously suspected.

A low surface free energy approach to FR coatings is based on the work of adhesion between a solid and a liquid as described by Dupre². The work of adhesion ($W_{ad} = \gamma_s + \gamma_l - \gamma_{sl}$), or work required to separate the liquid from the solid, is the sum of the surface free energies of liquid (γ_l) and solid (γ_s), minus the interfacial tension between the solid and liquid (γ_{sl}). A weaker adhesion results from lowering the surface free energy of the solid.

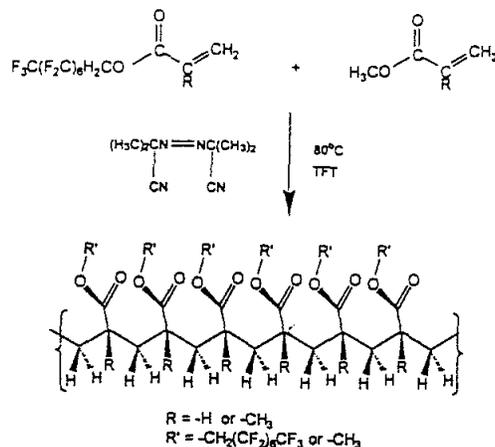
One objective of this work is to examine the effect of low surface free energy on the performance of FR coatings and to determine what other properties, such as surface stability, flexibility, or elasticity, might contribute toward the overall mechanism of fouling-release. For this purpose we have begun investigating perfluorinated acrylate copolymers through systematic variations of molecular structure, properties, and fluorine content. Here, we report the synthesis, characterization, and physical properties of these new low-surface-free-energy polymers.

RESULTS AND DISCUSSION

The synthetic work reported herein is a modification of previously described^{1,3,4} methods for preparing perfluorinated acrylate and methacrylate polymers. The monomer, 1H,1H-perfluorooctylacrylate (PFOA) is commercially available, but can be prepared in near quantitative yield from commercially available 1H,1H-perfluorooctanol. The solution polymerization reaction between PFOA and methylacrylate (MA) or methylmethacrylate (MMA) is shown schematically below, initiated by 2,2'-azobis-(2-methylpropanitrile), where the resulting copolymer stoichiometry is related to the relative reactivities and concentrations of the monomers in the reaction solution.

Synthetic Approach.

Our goal is to prepare polymers with predictably different polymer properties by varying molecular weight, composition, and molecular structure. Each of these variations have been optimized for co-monomer concentrations, temperature, solvent, reaction time, and reaction scale. Copolymerization was performed using only monomeric species (no prepolymerization) at elevated non-reflux temperatures under dry nitrogen with mechanical stirring. Reaction temperature was controlled and logged to computer. When necessary, gas chromatographic analysis of the reaction mixture was used to monitor extent of product formation.



Reproducibility issues in synthetic operations were addressed through utilization of automated syringe pumps for precise control over reagent addition rate. In addition, replicate syntheses of polymers were performed as a check for product inconsistencies.

Polymer molecular weight was controlled by varying the total monomer concentration in the reaction solution. High molecular weight materials ($>10^5$ g-mol⁻¹) were prepared in 1,3-bis(trifluoromethyl)benzene at high monomer concentrations and 20 hr reaction time. Low molecular weight polymers (10^4 - 10^5 g-mol⁻¹) were prepared in α,α,α -trifluorotoluene solvent at low monomer concentrations and 10 hr reaction time. Composition series of both low and high molecular weight polymers were prepared with 0%, 25%, 50%, 75%, and 100% total perfluoro-monomer concentration. Polymers within the high molecular weight composition series were prepared at constant target chain lengths, resulting in molecular weight variation. Low molecular weight polymers in the series were prepared at constant target molecular weights, resulting in chain length variation. Random and segmented copolymers were each prepared by controlling the relative proportions of co-monomer species present in the reaction solution by means of two methods respectively: 1) simultaneous addition of both monomers at concentrations derived from relative reactivity ratios of each co-monomer, and 2) addition of non-fluorinated monomer to all of the perfluorinated monomer in the initial solution. Copolymers produced using these two methods are illustrated for 50/50 PFOA/MA in Figure 1. All additions were performed continuously over the course of each reaction. Synthetic products were worked up by multiple precipitation into methanol and dried overnight *in vacuo* at -50°C .

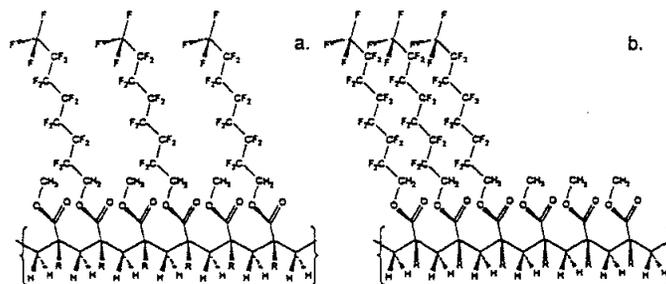


Figure 1. Random and segmented copolymers expected for 50/50 PFOA/MA (R = -H) prepared from different synthetic methods (see text).

Polymer Characterization

Molecular weights of synthetic products were determined by gel permeation chromatography using polystyrene standards as reference materials. Copolymer stoichiometry was confirmed using elemental analysis (Galbraith Laboratories, Inc.). These results indicate that method 1 polymers give expected compositions, unlike method 2 polymers which yield higher than expected perfluorooctylacrylate compositions. Elemental analyses are being confirmed for replicate synthetic products, however, for the purposes of this paper these results

are taken to provide an accurate measure of segmented (method 2) polymer compositions. These deviations in composition are bracketed in Table 1 for segmented PFOA/MA copolymers, where polymer type and composition are summarized with corresponding thermal property analyses from differential scanning calorimetry (DSC) results. Replicate DSC runs were performed on all polymer samples until consistent traces were obtained. Representative thermogram features are illustrated in Figure 2 for a series of high molecular weight random copolymers and both homopolymers. MA homopolymer thermograms typically exhibited a shifting glass transition between -10°C and $+10^{\circ}\text{C}$, because of synthesis difficulties (low solubility and difficult to control reaction kinetics) under reaction conditions similar to that used for perfluoro-copolymers. PFOA homopolymers showed uniform melting behaviors with only slight shifts in temperature. Though multiple phase behaviors were exhibited by some copolymers in each series, general trends were observable for both low and high molecular weight random copolymer series (LOMW- and HIMW-Random, respectively). Across each composition series, we observe uniform melting behavior at high PFOA content with a decrease in melting temperature and the appearance of a glass transition with increasing MA content. LOMW- and HIMW-Random copolymers show similar melting behaviors, but different Tg values with increased MA content. In general, a broad comparison of all composition series shows a depression in both melting and glass transition temperatures for random copolymers and high molecular weight copolymers.

Surface Properties.

Polymer surface energies for high molecular weight random and segmented copolymers were calculated from contact angles determined using a goniometer/microscope system equipped with a computer-interfaced CCD camera. Samples were cast from solution in a dust-free environment, dried under ambient conditions, and contact angles were measured with three test liquids at multiple (distinct) positions across the coating surface. Millipore-purified doubly distilled water (18 M Ω), hexadecane, and diiodomethane were used as test liquids. Surface energies were calculated using the method of Owens, Wendt, Rabel, and Kaelble⁵. The results of these measurements are shown in Table 2. These polymers exhibit very low surface free energies, in the range of 10-12 dyne-cm⁻¹. No clear trends were observed for polymers as a function of fluorine content or preparation method, even though surface energies are expected to decrease with increasing fluorine content. We are currently attempting to determine the reason for this unexpected result. Our initial rationale is that there are differences in surface roughness which can influence contact angle. In such a scenario, very small differences in surface roughness would likely be sufficient to scramble the surface energy ranking. A more detailed study to include surface roughness measurements is planned to investigate this further.

For comparison with the PFOA/MA copolymers described here, we have also prepared segmented and random low molecular weight methylmethacrylate copolymers with variable compositions. Our initial work with these copolymers indicates that PFOA/MMA copolymers can be synthesized in nearly the same manner, possess similar low surface free energies, but exhibit more complex thermal properties. Additionally, these polymers are being studied using solid state NMR spectroscopy (CP-MAS) for comparisons with data for PFOA/MA copolymers. These studies include relating differences in both number and intensity of resonances in spectra to the presence of varying amounts of fluorinated and non-fluorinated monomer units in the polymer backbone. The degree of molecular mixing along the polymer backbone is also being investigated using molecular relaxation (T₁ ρ) experiments. Results from these NMR investigations are being presented in a companion paper.⁶

Current and future efforts are focused on preparing uniform coatings of these polymer materials and evaluating their fouling-release properties. Particular attention is being directed at exploring surface properties of the coatings upon exposure to the marine fouling environment.

ACKNOWLEDGMENTS

This work was supported through the DoD-EPA-DOE Strategic Environmental Research and Development Program.

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Table 1. Copolymer compositions and thermal properties.

PFOA/MA Composition	LOMW-Segmented		LOMW-Random		HIMW-Segmented		HIMW-Random	
	Tg (C)	Tm (C)	Tg (C)	Tm (C)	Tg (C)	Tm (C)	Tg (C)	Tm (C)
25/75	25	43 [50/50]	-3		-1		-10	
50/50		41 [66/33]	15	25	15	39	-6	22
75/25		48 [70/30]		37		40		36
100/0		54		57				50

* Actual compositions noted in brackets if different from expected composition.

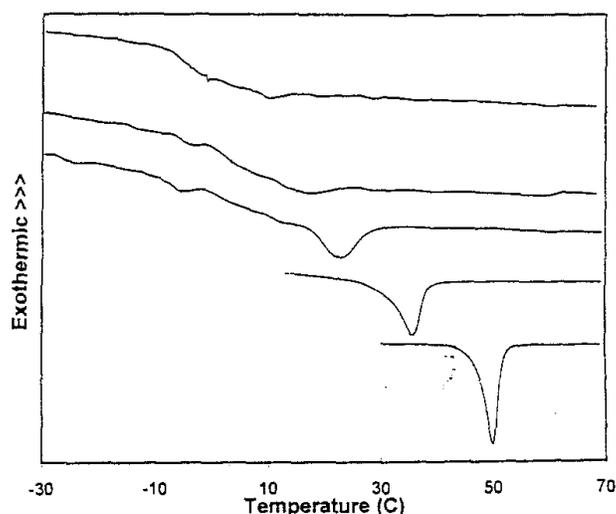


Figure 2. DSC data for random PFOA/MA copolymers (0, 25, 50, 75, 100 %PFOA, top to bottom trace respectively).

Table 2. Copolymer surface energies and contact angles.

PFOA/MA	Surface Energy	Contact Angle		
		Water	Hexadecane	Diiodomethane
HIMW Segmented Copolymers				
75/25	10.8	118.7	72.5	93.3
50/50	11.7	120.1	73.2	100.1
25/75	10.2	116.1	70.2	96.3
HIMW Random Copolymers				
100/0	12.4	122.7	73.3	96.4
75/25	11.6	122.8	72	97.3
50/50	10.8	119.1	70.5	98
25/75	11	120.4	72.3	88.6

PERFLUORINATED ACRYLATE AND METHACRYLATE FOULING-RELEASE POLYMERS. 1. SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

The motivation for this work is the development of new materials for non-polluting fouling-release (FR) coatings. Such coatings work by a property of the solid surface rather than toxicity of a released antifouling agent, thus, there is no risk of environmental pollution. The challenge in using non-toxic FR materials to solve fouling problems is to develop a coating which works well in all types of fouling environments, in the presence of both physical and chemical mechanisms of fouling organism attachment. Thus, the physico-chemical nature of FR materials and coating surfaces becomes increasingly important with respect to strength of organism attachment. Our approach takes advantage of the weak adhesion characteristics of low surface free energy materials. These materials have been prepared by incorporating perfluorinated alkyl sidechains onto a flexible polymer backbone to create comb-type polymers with low surface free energies. Our synthetic efforts have been designed for assessing the effect(s) of polymer physical properties on coating preparation, fouling performance, and cleaning behavior by using model polymers prepared from acrylate and methacrylate precursors. Emphasis has been placed on achieving consistent low surface free energies and fouling release properties by optimization of polymerization parameters. Issues of synthetic reproducibility and consistency, critical for correlating physical properties to FR performance, have been addressed through automation of key synthetic processes. This presentation will focus on polymer series prepared with systematic variations in copolymer type, sidechain composition, and molecular structure. Combined structure-property-performance studies of these polymers will be useful for determining the degree of fouling release which can be achieved without sacrificing coating toughness and durability.

INTRODUCTION

Straight-chain polymers with fluorinated sidegroups form a class of low surface-free-energy polymers which interact only weakly with polar liquids. Further, these materials are capable of withstanding harsh environmental conditions for extended periods of time. It has been shown that low surface free energy is a beneficial approach for materials which are to be used in marine fouling environments.¹ In such environments, marine fouling organisms produce bioadhesives which are secreted onto surfaces of substrata for purposes of initial attachment and subsequent fouling-organism colonization. Bioadhesion is a primary underlying mechanism which contributes directly to the problem of marine fouling. Previous and current solutions to this problem have predominantly included the use of anti-fouling coatings from which biocides are slowly released over time. This type of solution possesses an element of environmental risk and is the motivation for developing non-polluting, low-adhesion coatings, also referred to as fouling-release (FR) coatings, because fouling adheres only weakly and can be removed. Though it is apparent that low surface free energy is indeed a contributor to the mechanism of fouling-release, its exact role is still unclear, as is the role of other coating properties which are perhaps more critical than previously suspected.

A low surface free energy approach to FR coatings is based on the work of adhesion between a solid and a liquid as described by Dupre² and shown in (1).

$$W_{sl} = \gamma_s + \gamma_l - \gamma_{sl} \quad (1)$$

The work of adhesion or work required to separate the liquid from the solid (W_{sl}), is the sum of the surface free energies of liquid (γ_l) and solid (γ_s), minus the interfacial tension between the solid and liquid (γ_{sl}). A weaker adhesion results from lowering the surface free energy of the solid. However, simply lowering the surface free energy is not sufficient. For example, experimental results with PTFE show that fouling still occurs with strong adhesion. This can be rationalized by comparison of the critical surface tension³ of the PTFE solid ($\sim 18 \text{ dyne-cm}^{-1}$) with the surface tension of liquid barnacle adhesive in seawater (12 dynes-cm^{-1})¹. Because PTFE has a larger critical surface tension than the surface tension of the liquid barnacle adhesive, barnacles can adhere to the PTFE surface. To defeat adhesion by low surface tension liquids such as barnacle cement, the target surface free energy must therefore be less than 12 dyne-cm^{-1} . This simple hypothesis has led to investigations of low surface energy materials by our laboratory and others.

Extremely-low free-energy surfaces can be obtained by adsorbing monolayers of perfluorinated materials onto solid substrates, however, this is very impractical for coating applications. More useful systems have been successfully demonstrated in our laboratory by addition of perfluorinated surfactant additives to polymers or by preparation of comb-like polymers with siloxane, polyacrylate, and polymethacrylate backbones with perfluorinated long sidechains.¹ The use of additives resulted in low surface free energy materials, but this approach was abandoned because of

susceptibility to molecular reorientation upon exposure to water, which would lead to a surface free energy increase. Although costly, perfluorinated siloxanes exhibited excellent performance and properties. Perfluorinated acrylate and methacrylate homopolymers were prepared and exhibited low surface free energies, but these polymers exhibited undesirable physical properties. Relative to the homopolymers, perfluorinated copolymers showed much lower than expected surface free energies with much-improved physical properties and are more economically feasible.

One objective of this work is to examine the effect of low surface free energy on the performance of FR coatings and to determine what other properties, such as surface stability, flexibility, or elasticity, might contribute toward the overall mechanism of fouling-release. For this purpose we have begun investigating perfluorinated acrylate copolymers through systematic variations of molecular structure, properties, and fluorine content. Here, we report the synthesis, characterization, and physical properties of these new low-surface-free-energy polymers.

EXPERIMENTAL DETAILS

All syntheses were performed in reactors equipped with mechanical stirring, ports for introduction of reagents and inert gas, temperature probes for logging reaction temperature, and automated syringe pumps for introduction of reagents into the reaction pot. Reagent additions were performed continuously over the course of each reaction. All solvents were distilled immediately prior to use. Synthetic products were worked up by multiple precipitation into methanol and dried overnight *in vacuo* at $\sim 50^{\circ}\text{C}$. Gas chromatographic analyses during the reaction were performed by quenching aliquots of the reaction mixture with excess Br_2 , followed by reaction of the remaining Br_2 with cyclohexene prior to injection onto the column. Transmission infrared spectra were collected either on NaCl salt plates or in KBr pellets. Polymer molecular weights were characterized with gel permeation chromatography in either α,α,α -trifluorotoluene or 1,3-bis(trifluoromethyl)benzene using polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed on 5-10 mg samples of each polymer beginning at either liquid nitrogen temperatures or ice water temperatures. DSC runs were cycled for all polymer samples until consistent traces were obtained.

Solid state CP-MAS NMR spectra were collected using a Bruker MSL-200 spectrometer operating at 50.323 Mhz for ^{13}C and 200.13 Mhz for ^1H . A 7mm DB/MAS probe was employed. Because powdering was not possible for these samples, it was necessary to use inserts made of Kel-F[®] to effect spinning.⁴ Typical spinning speeds were 4.4 kHz and a ^1H decoupling field strength of 50 kHz was used. Pulse lengths for ^1H and ^{13}C were 5 μs and typical relaxation delays were 5 s. The ^1H spin-lattice relaxation time in the rotating frame ($T_{1\rho}^{\text{H}}$) was measured by spin-locking the ^1H magnetization prior to cross polarization to the ^{13}C -nuclei. A spin-locking field 50 kHz was used and contact times were in the range 250 μs to 10 ms. All spectra were referenced to TMS using adamantane as a secondary reference.

the extent of product formation. Consistency and reproducibility in synthetic operations were addressed through utilization of automated syringe pumps for precise control over reagent addition rate. In addition, replicate syntheses of polymers were performed as a check for product inconsistencies.

Polymer molecular weight was controlled by varying the total monomer concentration in the reaction solution. High molecular weight materials ($>10^5$ g·mol⁻¹) were prepared in 1,3-bis(trifluoromethyl)benzene at high monomer concentrations and 20 hr reaction time. Low molecular weight polymers (10^4 - 10^5 g·mol⁻¹) were prepared in α,α,α -trifluorotoluene solvent at low monomer concentrations and 10 hr reaction time. Composition series of both low and high molecular weight polymers were prepared with 0%, 25%, 50%, 75%, and 100% total perfluoro-monomer concentration. Polymers within the high molecular weight composition series were prepared at constant target chain lengths, resulting in molecular weight variation. Low molecular weight polymers in the series were prepared at constant target molecular weights, resulting in chain length variation. Random and segmented copolymers were each prepared by controlling the relative proportions of co-monomer species present in the reaction solution by means of two methods respectively: 1) simultaneous addition of both monomers at concentrations derived from relative reactivity ratios of each co-monomer, and 2) addition of non-fluorinated monomer to all of the perfluorinated monomer in the initial solution. Example copolymers produced using these two methods are schematically illustrated for 50/50 PFOA/MA in Figure 1.

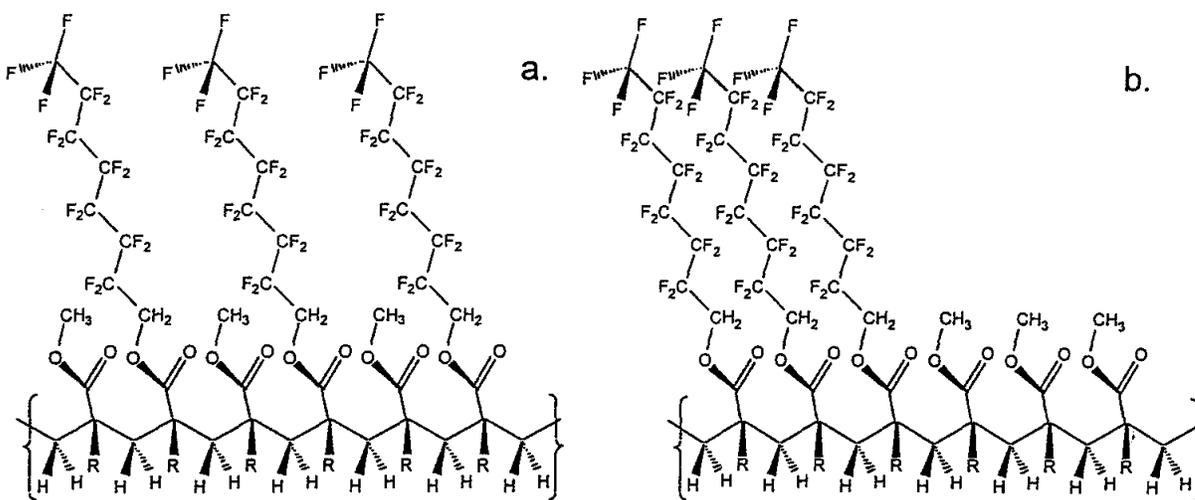


FIGURE 1. Illustrations of a) Random and b) segmented copolymers expected for 50/50 PFOA/MA (R = -H) prepared from different synthetic methods (see text).

POLYMER CHARACTERIZATION

Elemental analysis data indicate that method 1 polymers give expected compositions, unlike method 2 polymers which yield higher than expected perfluorooctylacrylate compositions. Elemental analyses are being confirmed for replicate synthetic products, however, for the purposes of this paper these results are

taken to provide an accurate measure of segmented (method 2) polymer compositions. These deviations in composition are bracketed in Table 1 for segmented PFOA/MA copolymers, where polymer type and composition are summarized with corresponding thermal property analyses from differential scanning calorimetry (DSC) results.

TABLE 1. Copolymer compositions and thermal properties.

PFOA/MA Composition	LOMW-Segmented		LOMW-Random		HIMW-Segmented		HIMW-Random	
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50/50		41 [66/33]	15	25	15	39	-6	22
75/25		48 [70/30]		37		40		36
100/0		54		57				50

* Actual compositions noted in brackets if different from expected composition.

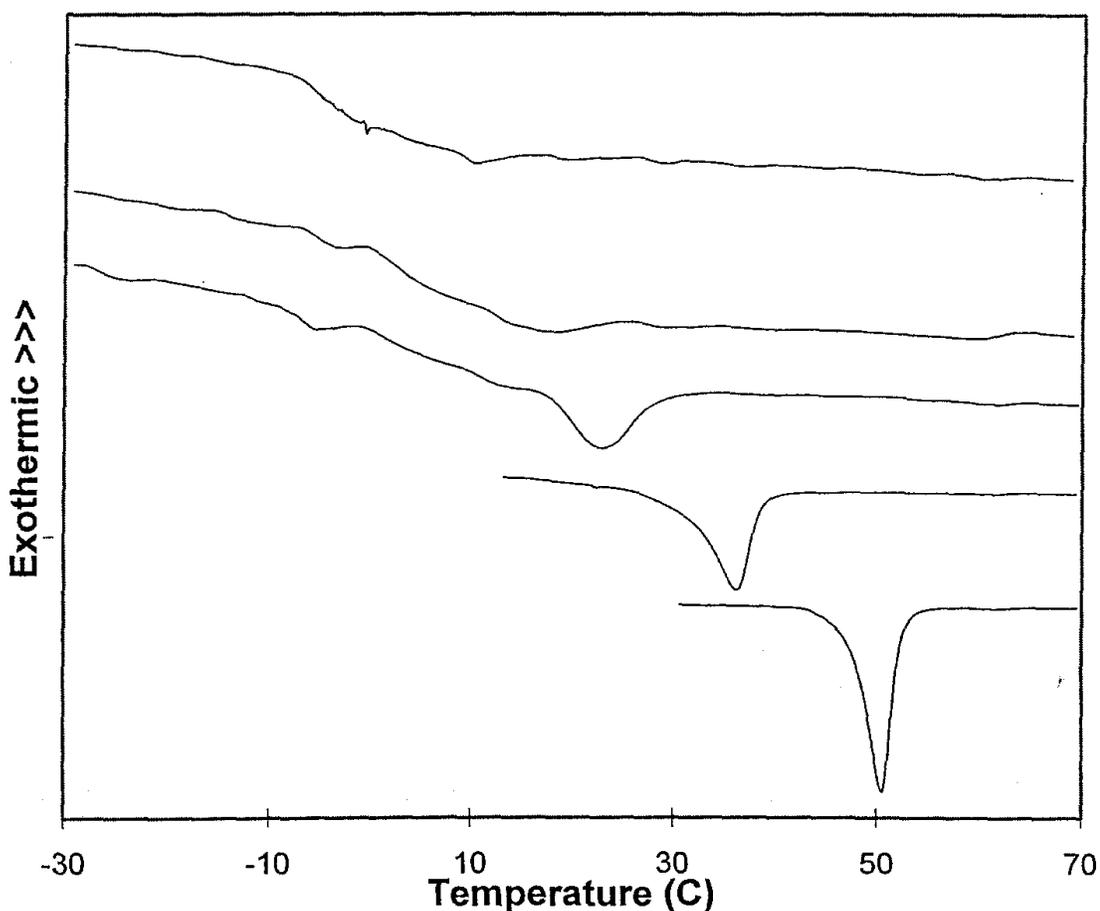


FIGURE 2. DSC data for random PFOA/MA copolymers (0, 25, 50, 75, 100 %PFOA, top to bottom trace respectively).

Representative DSC thermogram features are illustrated in Figure 2 for a series of high molecular weight random copolymers and both homopolymers. MA homopolymer thermograms typically exhibited a shifting glass transition temperature (T_g) between -10°C and $+10^\circ\text{C}$, because of synthesis difficulties (low solubility and difficult to control reaction kinetics) under reaction conditions similar to that used for perfluoro-copolymers. PFOA homopolymers showed uniform melting behaviors with only slight shifts in temperature. Though multiple phase behaviors were exhibited by some copolymers in each series, general trends were observable for both low and high molecular weight random copolymer series (LOMW- and HIMW- Random, respectively). Across each composition series, we observe uniform melting behavior at high PFOA content with a decrease in melting temperature and the appearance of a glass transition with increasing MA content. LOMW- and HIMW-Random copolymers show similar melting behaviors, but different T_g values with increased MA content. In general, a broad comparison of all composition series shows a depression in both melting and glass transition temperatures for random copolymers and high molecular weight copolymers.

NMR RELAXATION STUDIES

In Figure 3, ^{13}C CP/MAS spectra of 100/0 PFOA/MA (PFOA homopolymer), 0/100 PFOA/MA (MA homopolymer), and the three intermediate copolymers (25/75, 50/50, and 75/25 PFOA/MA) are shown. The peak near 40 ppm is an overlap of PFOA and MA resonances of mainchain carbons. The sharp resonance at 52 ppm is the methoxy carbon of MA and the resonance at 59 ppm corresponds to $-\text{CH}_2$'s in the PFOA sidechain. The broad feature near 120 ppm corresponds to $-\text{CF}_2$ in the PFOA sidechain. Lastly, the peak at 175 ppm is an overlap of resonances of carbonyl carbons from both PFOA and MA. These spectral data show differences which are consistent for increasing amounts of PFOA relative to MA in the copolymers.

A typical set of $T_{1\rho}^{\text{H}}$ relaxation data is shown in Figure 4 for a 50/50 PFOA/MA copolymer blend. The relaxation behaviors of four of the resonances were followed as indicated in the legend. The peak at 120 ppm is too broad to allow for analysis. The lines of best fit and the corresponding $T_{1\rho}^{\text{H}}$'s for each line are also included in the plot. From these data, it is clear that all of the peaks relax at essentially the same rate. The slopes agree within 6% of the average. This similarity in relaxation times results from rapid spin-diffusion, which averages the relaxation times of the various components. These data indicate that the components in this sample are homogeneously mixed to a distance of approximately 20 Angstroms.⁷ If this mixing was not present, the individual resonances would tend to relax at rates similar to those of the corresponding homopolymer.⁸

Relaxation results for the two homopolymers of PFOA and MA, and the intermediate copolymers are reported in Table 2. $T_{1\rho}^{\text{H}}$'s are reported for the peak at 175 ppm (carbonyl), 59 ppm (PFOA only), and 52 ppm (MA only). The average $T_{1\rho}^{\text{H}}$ and scatter, calculated from all the relaxation curves of all the peaks is also included in the Table. The scatter provides an indication of how similar the slopes are for each sample and are seen to deviate by 12% at most, though generally much less. Since

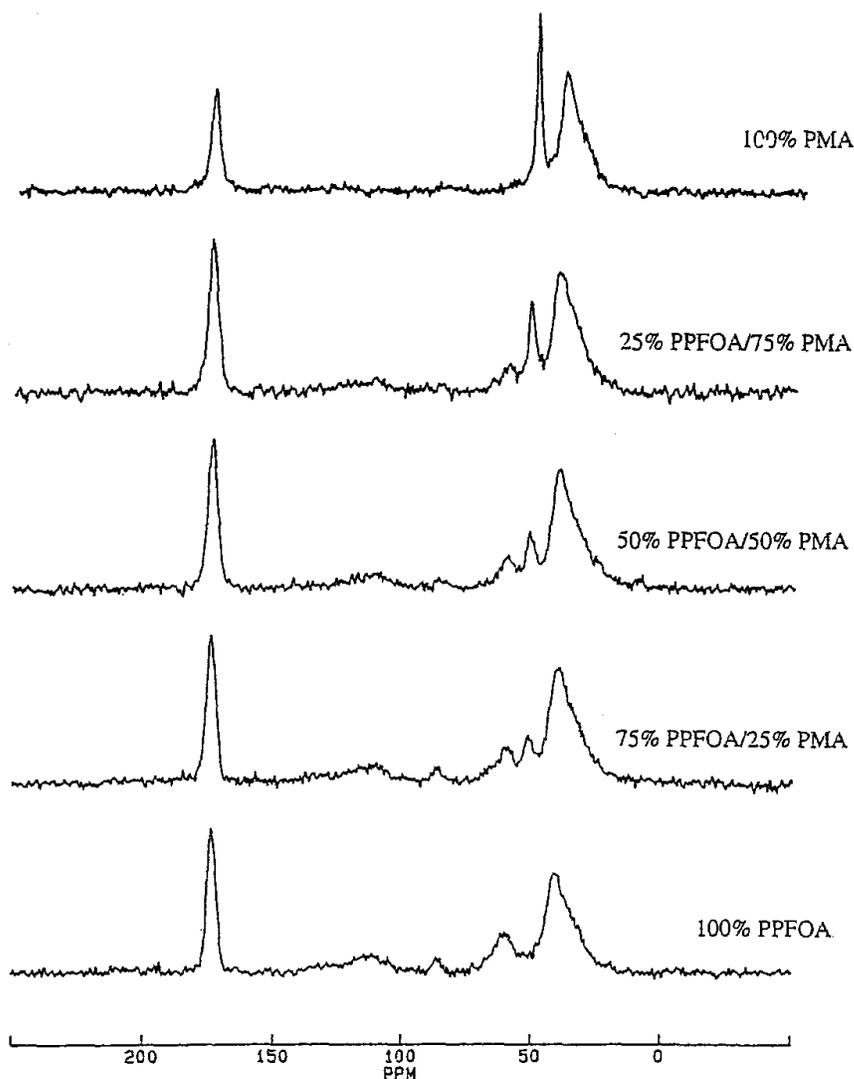


FIGURE 3. ^{13}C CP/MAS NMR spectra for a series of five PFOA/MA polymers.

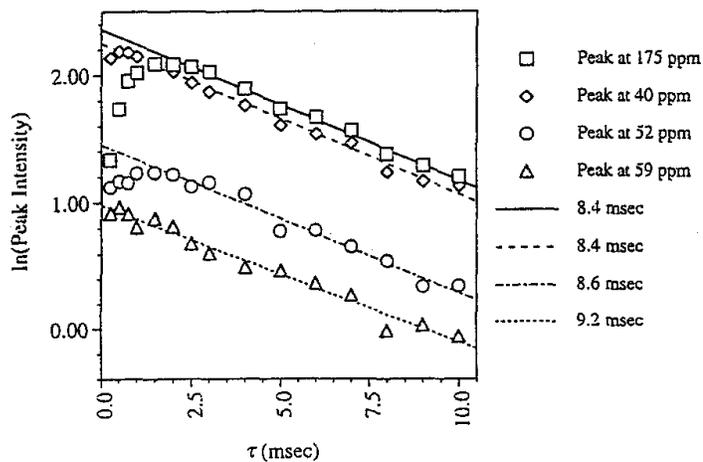


FIGURE 4. $T_{1\rho}^H$ relaxation data for a 50/50 PFOA/MA copolymer.

TABLE 2. $T_{1\rho}$ values (in ms) for a series of five PFOA/MA copolymers.

Blend	$T_{1\rho}$ (C=O) ^a	$T_{1\rho}$ (PPFOA) ^b	$T_{1\rho}$ (PMA) ^c	$T_{1\rho}$ (ave) ^d	Scatter (%) ^e
100% PPFOA	16.1	15.6	—	15.8	2
75% PPFOA/25% PMA	12.9	15.8	16.3	14.7	12
50% PPFOA/50% PMA	8.4	9.2	8.6	8.7	6
25% PPFOA/75% PMA	8.1	7.4	7.4	7.5	8
100% PMA	4.3	—	4.3	4.3	1

a From peak at 175 ppm.

b From peak at 59 ppm.

c From peak at 52 ppm.

d From all peaks.

e Largest % error of any $T_{1\rho}$ from $T_{1\rho}$ (ave).

some of the resonances are broadened and present at a level of only 25%, it is easily understood how this error is introduced. It is expected that the carbonyl data are the most reliable, since this peak is more narrow and intense than all other peaks in the spectra, with the exception of the methoxy peak in the spectrum of the MA homopolymer.

A plot of the $T_{1\rho}^H$ curves and lines of best fit for the five samples are shown in Figure 5, for data from the carbonyl peak at 175 ppm. From this plot, it is clear that the various copolymers exhibit $T_{1\rho}^H$ values that are intermediate between those of the homopolymers. This is further evidence of intimate mixing of the two components. In addition, the trend of decreasing $T_{1\rho}^H$ values as the %MA is increased is very obvious, supporting the concept of a high degree of component miscibility. It should be noted that while the carbonyl peak is an overlap of two resonances, all other resonances in the spectra, including the non-overlapping resonances at 52 ppm and 59 ppm, display the same trends.

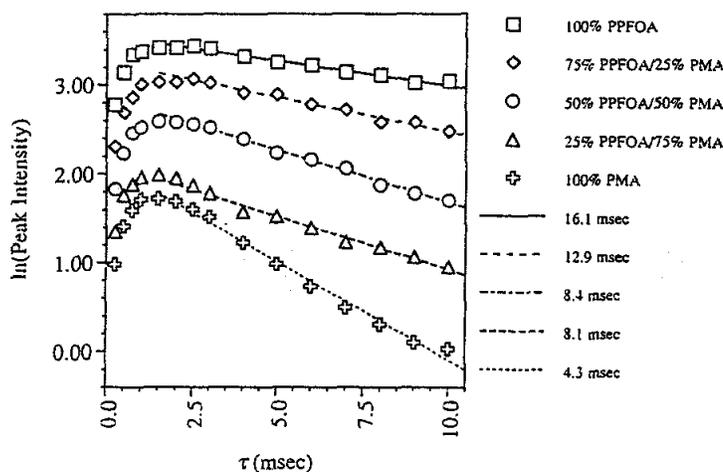


FIGURE 5. $T_{1\rho}^H$ curves for a series of five PFOA/MA copolymers measured using the carbonyl resonance at 175 ppm.

SURFACE PROPERTIES.

Polymer surface energies for high molecular weight random and segmented copolymers were calculated from contact angles, measured with three test liquids at multiple (distinct) positions across the coating surface, using the method of Owens, Wendt, Rabel, and Kaelble⁹. The results of these measurements are shown in Table 3. These polymers exhibit very low surface free energies, in the range of 10-12 dyne-cm⁻¹. No clear trends were observed for polymers as a function of fluorine content or preparation method, even though surface energies are expected to decrease with increasing fluorine content. We are currently attempting to determine the reason for this unexpected result. Our initial rationale is that there are differences in surface roughness which can influence contact angle. In such a scenario, very small differences in surface roughness would likely be sufficient to scramble the surface energy ranking. A more detailed study to include controlled surface preparation combined with surface roughness measurements is planned.

TABLE 3. Copolymer surface energies and contact angles for coatings cast from 30 cP polymer solutions.

PFOA/MA	Surface Energy	Water	Hexadecane	Diiodomethane
		Contact Angle	Contact Angle	Contact Angle
HIMW Segmented Copolymers				
75/25	10.8	118.7	72.5	93.3
50/50	11.7	120.1	73.2	100.1
25/75	10.2	116.1	70.2	96.3
HIMW Random Copolymers				
100/0	12.4	122.7	73.3	96.4
75/25	11.6	122.8	72	97.3
50/50	10.8	119.1	70.5	98
25/75	11	120.4	72.3	88.6

PFOA/MMA COPOLYMERS

For comparison with the PFOA/MA copolymers described here, we have also prepared segmented and random low molecular weight methylmethacrylate copolymers with variable compositions. Our initial work with these copolymers indicates that PFOA/MMA copolymers can be synthesized in nearly the same manner, possess similar low surface free energies, but exhibit more complex thermal properties. Additionally, these polymers are being studied using solid state NMR spectroscopy (CP-MAS) for comparisons with data for PFOA/MA copolymers.

SUMMARY AND CONCLUSIONS

New low surface free energy FR polymers have been prepared with systematic variations in fluorine composition, copolymer type, molecular structure, and molecular weight. All of the fluorine-containing polymers exhibit the low surface free energies required for fouling release. NMR studies indicate that the copolymers are homogeneous and fully dispersed on a scale of approximately 20 Angstroms. These

polymers exhibit a significant range of physico-chemical properties to prepare a battery of coatings for systematic studies of fouling and cleaning efficacy. Current efforts with these polymers are focused on preparing uniform coatings and evaluating their fouling-release properties; for which preliminary data are presented in a companion paper.¹⁰ Particular attention is currently being directed at the surface properties of these coatings upon exposure to the marine fouling environment.

ACKNOWLEDGMENTS

This work is supported through the DoD-DOE-EPA Strategic Environmental Research and Development Program. K.L.A. is supported by an ONR/ASEE postdoctoral fellowship.

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**PERFLUORINATED ACRYLATE AND METHACRYLATE FOULING-RELEASE
POLYMERS. 2. COATING PREPARATION, CHARACTERIZATION, AND
PROPERTIES**

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ABSTRACT

Historically, toxic coating systems have been an efficient solution to the centuries-old problem of fouling by marine organisms. Using non-toxic materials to achieve similar results ultimately requires that the coating resist both physical and chemical attachment in all fouling environments. Non-toxic, fouling-release (FR) polymers form coatings which work by minimizing the adhesive properties of the surface, leading to fouling organism attachment with low adhesion strength, a parameter directly related to coating cleanability. Our coatings work is directed toward determination of critical physical and chemical parameters of new FR fluoropolymer coatings and their correlation with fouling release. Important polymer/coating parameters include molecular structure and composition, physical properties, coating preparation, surface energetics (static and dynamic), and surface structure/stability. Reproducibility and consistency in polymer preparation, coating application and testing, and performance evaluation are essential for accurate comparisons and meaningful correlations. The interrelationships between polymer and coating properties and their possibly combined effects on fouling behavior are determined for developing and optimizing the coating system. In this work, coating preparation, coating and polymer properties, and fouling release behaviors for perfluorinated acrylate-based FR polymers, described in a companion paper, have been investigated. Structure-property-performance correlations with determined critical polymer and coating parameters will be presented.

INTRODUCTION

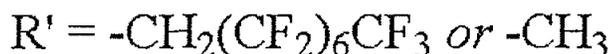
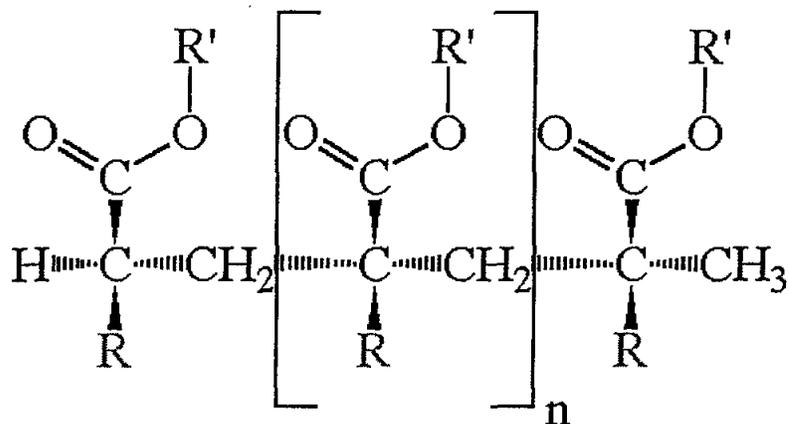
Straight-chain polymers with fluorinated sidegroups form a class of low surface-free-energy polymers which interact only weakly with polar liquids. Further, these materials are capable of withstanding harsh environmental conditions for extended periods of time such as that found in marine fouling environments. In the fouling environment, marine organisms produce bioadhesives which are secreted onto surfaces of substrata for purposes of initial attachment and subsequent fouling-organism colonization. Bioadhesion is a primary underlying mechanism which contributes directly to the problem of marine fouling. Previous and current solutions to this problem have utilized anti-fouling coatings from which biocides are slowly released over time. This type of solution possesses an element of environmental risk and is the motivation for developing non-polluting, low-adhesion coatings, also referred to as fouling-release (FR) coatings. In such coatings, fouling adheres only weakly and can be removed. Though it is apparent that low surface free energy is indeed a contributor to the mechanism of fouling-release the role of other coating properties which are perhaps more critical than previously suspected is of interest in this work.

Our approach utilizes low surface free energy as a basis for FR coatings as described in a companion paper¹ on synthesis and characterization of new FR polymer materials, and is based on minimizing the work of adhesion between a solid surface and a liquid bioadhesive. The objectives of the work described here are to examine the effect of low surface free energy on the performance of FR coatings and to determine what other properties, such as surface stability, flexibility, or elasticity, might contribute toward the overall mechanism of fouling-release. For this purpose, we prepared perfluorinated acrylate copolymers through systematic variations of molecular structure, properties, and fluorine content as described in Paper 1.¹ Herein, we report the coating preparation, properties, fouling-release efficacy, and performance features of these new low-surface-free-energy polymers.

EXPERIMENTAL DETAILS

A generalized structure of the polymers investigated in this work is shown below. Experimental data reported here are for homopolymers and copolymers prepared from perfluorooctylacrylate (PFOA) and methylacrylate (MA) or methylmethacrylate (MMA). Experimental details of the syntheses are described in Paper 1.¹ Systematic variations for the polymers used in these studies include low and high molecular weight (referred to as LOMW and HIMW) random and segmented polymers with the following PFOA/MA and PFOA/MMA compositions: 100/0, 75/25, 50/50, 25/75, 0/100. Coatings have been prepared from these formulations as a function of spray solution viscosity. The resulting matrix of systematically varied coatings were then utilized for surface characterization and FR evaluation studies.

For coating preparations, a DeVilbiss AGX-550 automatic spray gun converted for High Volume Low Pressure (HVLP) applications was used to spray Formula-150 (F-150) epoxy-polyamide primer (Pro-Line Paint Co.) and polymer solutions. A DeVilbiss AGXV-400 sprayhead assembly and JGHV-101-33A air cap was used for the HVLP



conversion. Standard F-150 paint was sprayed using a 0.042 in. fluid tip and needle set (AGX-4402-FX). A tip size of 0.028 in. (AGX-4402-G) was used for application of lower viscosity polymer solutions. The spray gun is mounted on vertical rails with a positioning range of 8 in. The sample substrate holder is mounted on horizontal rails and is programmed to pass through the spray gun paint-fan at precisely controlled distances and speeds. Movement of the sprayer and sample holder is attained by miniangle stepper motor-belt systems (Minelea Co. Ltd.) controlled by an Arrick Robotics MD-2 dual stepper motor driver. System control is through application software written in Visual Basic (ver. 3.0, Microsoft Corp.) running on a 486-33MHz PC. Positioning of the spray gun and sample holder occur in increments of 0.05 in. and speeds of 0.08 in.-sec⁻¹ to 2.50 in.-sec⁻¹. Samples for fouling evaluation consisted of 0.25 in. diameter fiberglass rods cut into 11 cm lengths and coated with F-150 to provide a practical undercoat upon which the test coating could then be applied. Up to nineteen rods can be mounted in the rod holder assembly which positions each individual rod vertically in front of the sprayer at a rotation speed calculated for complete and even coverage of the rod. Rotation of the rods is through a motor driven gear assembly powered by an independent power source. The rod center to center separation is 0.3125 in., thereby minimizing the amount of paint lost to dead space. Typical spraying parameters for F-150 application were; paint feed pressure = 23 psi, air cap feed pressure = 25 psi, sprayer to substrate distance = 7 in., needle adjustment knob opened 3 complete turns, sprayer stroke speed = 0.5 in.-sec⁻¹ and rod rotation rate = 30 RPM. Typical spraying parameters for polymer solutions were; paint feed pressure = 20 psi, air cap feed pressure = 20 psi, sprayer to substrate distance = 4.5 in., needle adjustment knob opened 3 complete turns, sprayer stroke speed = 0.5 in.-sec⁻¹ and rod rotation rate = 40 RPM. During application of the polymer solutions, these parameters were optimized for flow rate through the sprayer and uniform

coverage of the sample. Typically one sprayer pass was sufficient to cover 9 cm of the rod with the either F-150 or polymer. The flat end of the rod, though not evaluated in coating studies, was painted manually with a small artist's brush to preclude fouling growth onto the test surface during fouling evaluation. Following coating application, the rods were suspended and allowed to dry under ambient conditions. The rods were stored in this manner until used.

A Brookfield Model DV II+ viscometer with a UL 316 s/s spindle assembly (Part no. ULA-ZY) was used to measure viscosities of polymer spray solutions. An alternate spindle set (LV) was used to measure the higher viscosity F-150 primer paint. Calibration of the instrument was performed with Brookfield silicone oil viscosity standards.

A Dektak profilometer (Dektak 3 ST Version 1.07) scanning over a length of 50000 um was used for spray-fan profile optimization and to measure roughness of coated rods. The stylus force was 10 mg and the number of data points was set at 8000. For rod sample data, gross periodic features due to the spray fan profile were subtracted out and analyzed separately from microscopic roughness features.

RESULTS AND DISCUSSION

COATING PREPARATION

Properties critical to spray-coating these materials are related to solubility and viscosities of different polymer formulations. Prior to applying coatings onto appropriate sample coupons, viscosity parameters were evaluated for each polymer formulation and are summarized in Table 1. The objective of spraying these materials as opposed to other means of coating preparation is to control the surface physical and chemical properties of the coating and prepare surfaces whereby it is possible to gain insight into effects of these properties on FR performance. As an initial approach, we have sought

TABLE 1. Solution concentrations and viscosities for HIMW Random and Segmented copolymers used in fouling evaluation studies.

PFOA/MA	HIMW-Semented		HIMW-Random	
	Conc. mg/mL	Viscosity (cP)	Conc. mg/mL	Viscosity (cP)
25/75	0.3958	32.9	0.4946	30.6
	0.5555	84.7	0.748	81.0
	0.6682	133.6	0.8663	129.6
50/50	0.4312	32.4	0.6499	29.2
	0.6207	85.0	1.002	78.0
	0.701	132.2	1.142	131.0
75/25	0.4455	29.9	0.7919	29.6
	0.7219	83.6	1.163	82.3
	0.8131	132.2	1.339	130.8
100/0	0.80572	27.3		
	1.245	82.5		
	1.427	130.8		

to prepare a matrix of coatings with systematic variation in polymer type, fluorine content, and spray-viscosity. Because spray-viscosity is directly related to concentration of the polymer in solution, viscosity variations are expected to produce coatings with differing degrees of crystallinity. It is our intention to control the physical and chemical homogeneity at the coating surface using this approach.

Spraying parameters, including sample orientation, rotation speed, spray-head speed, and feed pressure, were individually optimized for each type of coating. Coating solutions were sprayed onto substrates using these optimized parameters until a uniform coverage of material was present on each sample coupon. Resultant coating thicknesses ranged from 75 μm to 200 μm . When all variables except for viscosity are kept constant, surface features are directly dependent upon the behavior of the materials at different concentrations in solution. For a given material, a high viscosity should produce a more glassy morphology whereas, a low viscosity should produce a more crystalline morphology. For the coatings investigated here, comparisons can then be made within the variable matrix (polymer type, fluorine content, and spray-viscosity) for coatings in which two of these parameters remain constant.

COATING CHARACTERIZATION

During sprayer optimization, surface profilometry measurements were utilized to determine the gross pattern of variation across the spray profile. By mapping a flat test sample, it was possible to determine the most uniform areas of the spray, and develop a systematic optimization procedure to produce a highly uniform coating. An example of this is shown in Figure 1. The coating was mapped over the spray fan of 6 in. by the distance travelled of 2 in. The z-axis reflects a very small variation in feature height of only 1-2 μm over this area, observed as a slight bulge or increased amount of material in the center of the profile, uniform and centered over a distance of ~ 4 in. This type of optimization procedure was performed for each viscosity and variation in spray conditions prior to spraying sample rods.

After coating the sample rods to be used in performance evaluations, the surface roughness of each coating was evaluated using profilometry. Surface roughness as a function of spray viscosity for each coating type is shown in Figure 2. Significant variation from one material to the next was observed in addition to significant differences upon increasing the spray viscosity. The gross features of all rod samples consistently exhibited shallow peak and valleys on the order of 1-2 μm in height and 0.5-1 cm peak-to-peak. Surface roughness was derived from these data by subtracting out the gross sprayer features and analyzing the remaining microscopic features separately. This microscopic surface roughness parameter will become significant when making correlations to FR performance.

Water contact angles were measured for polymers spray-coated onto rod samples. These data are shown in Figure 3 for random and segmented HIMW polymers sprayed from 30 cP solutions. Both polymer types reflect an increasing contact angle with fluorine content. Upon comparison of the data in these two figures, slight variations are also noted between random and segmented polymers sprayed at the same viscosity. Comparison of sprayed sample data with cast samples¹ shows a

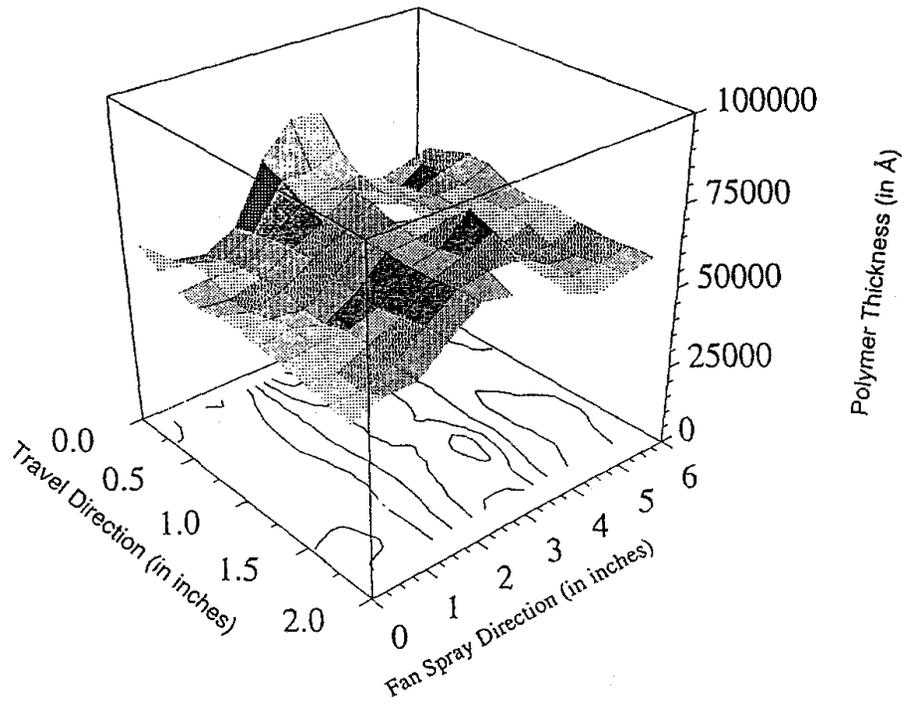


FIGURE 1. Profilometry mapping of a test sample used for optimization of the HVLP sprayer system.

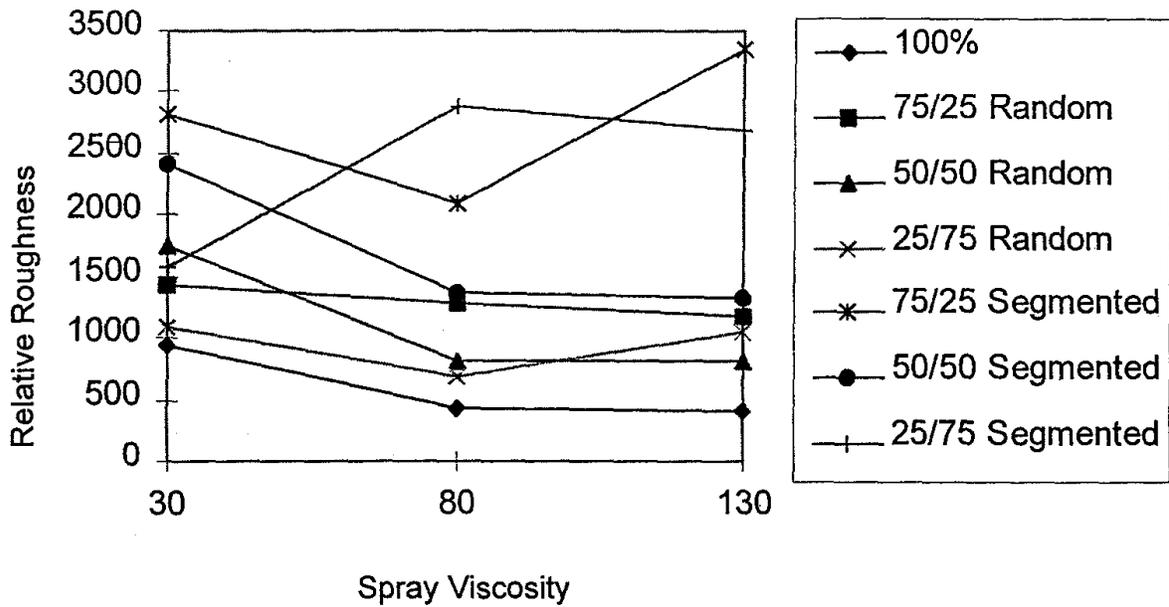


FIGURE 2. Representative surface roughness measured by profilometry for polymer formulations sprayed at different viscosities.

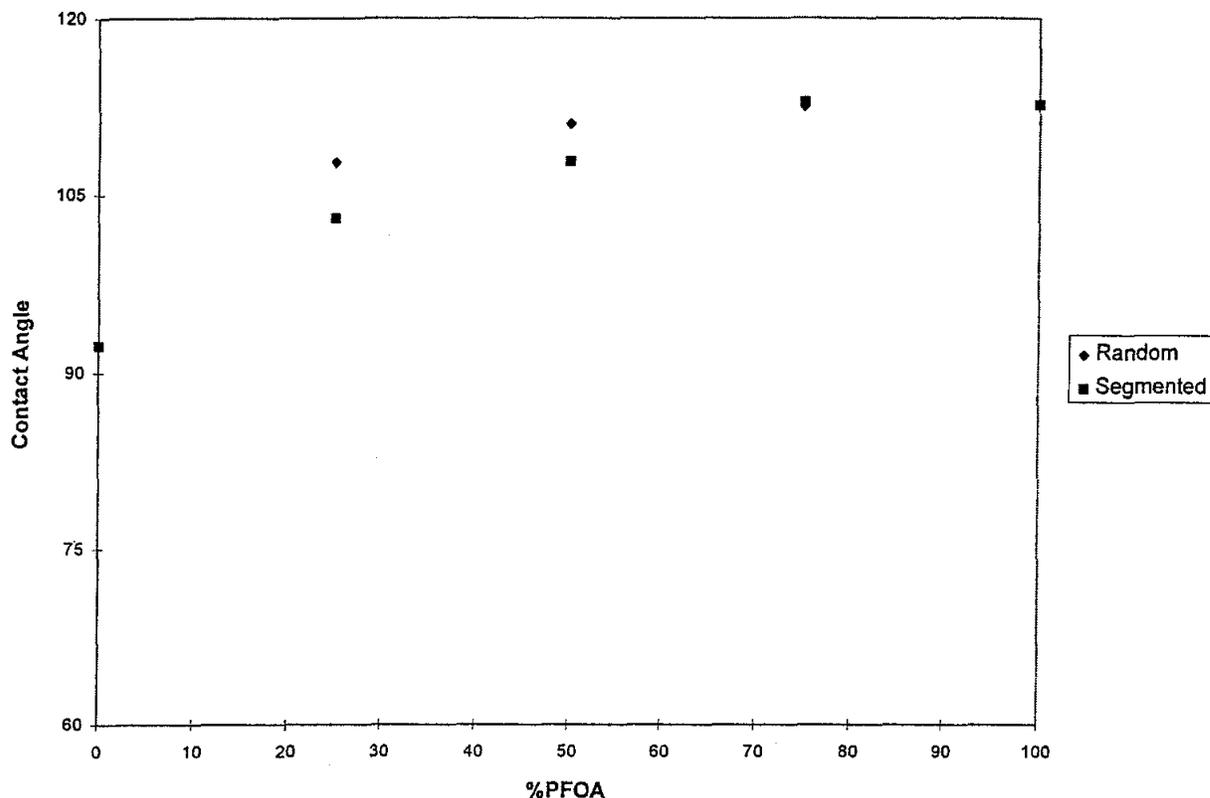


FIGURE 3. Water contact angles for a) HIMW-Random and b) HIMW-Segmented copolymers coated on sample rods.

slight decrease in water contact angle for coated rods. This decrease is attributed to drop deformation induced by the curved surface of the rod.

FOULING STUDIES

Replicates of each type of coating were evaluated in San Diego Bay during the summer fouling season (June-October). Samples were fouled for 28 day periods, after which fouling behaviors were evaluated at the species level. Measured parameters included biomass and species coverage (area). Cleaning efficiency was calculated from normalized coverage difference measurements before and after samples were cleaned using a jet of water from a Water Pik apparatus. Preliminary results from these studies are shown in Figures 5-8. One coating failure (peeling) was noted for the 75/25 PFOA/MA random copolymer, indicative of poor inter-coat adhesion. The total fouling data in Figure 5 do not take into account differences in the type of fouling present on samples. However, data in Figures 6-8 are presented for individual species and are thus directly comparable. A plot of average cleaning efficiency, shown in Figure 9, corresponds to an average of the data for each coating from Figures 6-8. Currently, these cleaning data are being used for correlations with coating chemical and physical properties to determine the significance and interdependencies of differences observed for these coating variations.

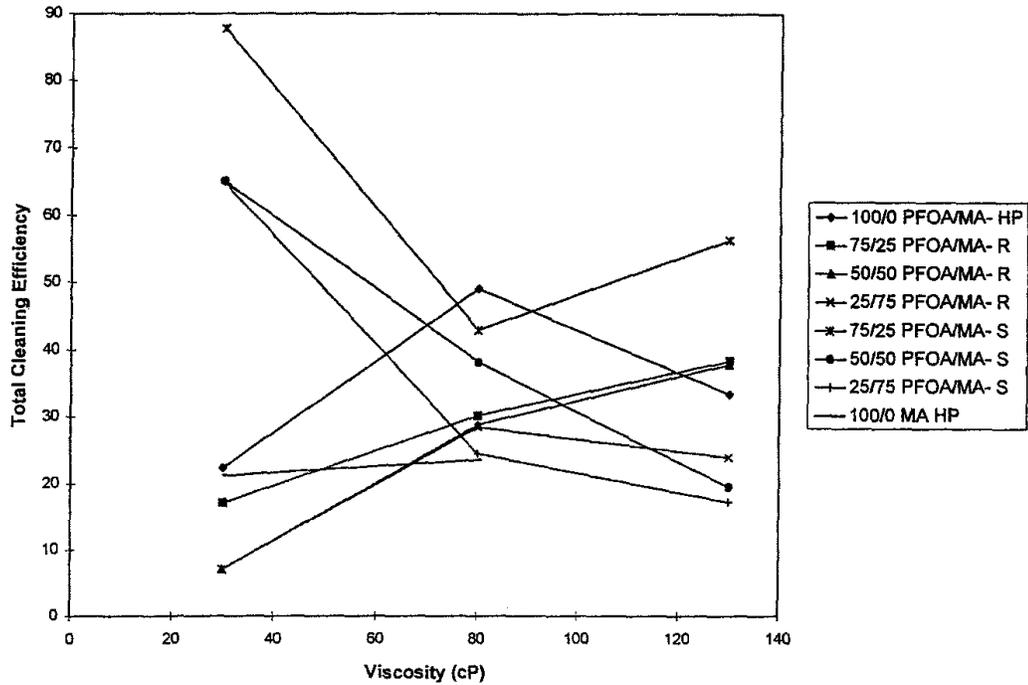


FIGURE 5. Cleaning efficiencies (% relative to control) derived from total fouling (all species) for HIMW random (R) and segmented (S) copolymer (CP) and homopolymer (HP) coatings prepared from different solution viscosities.

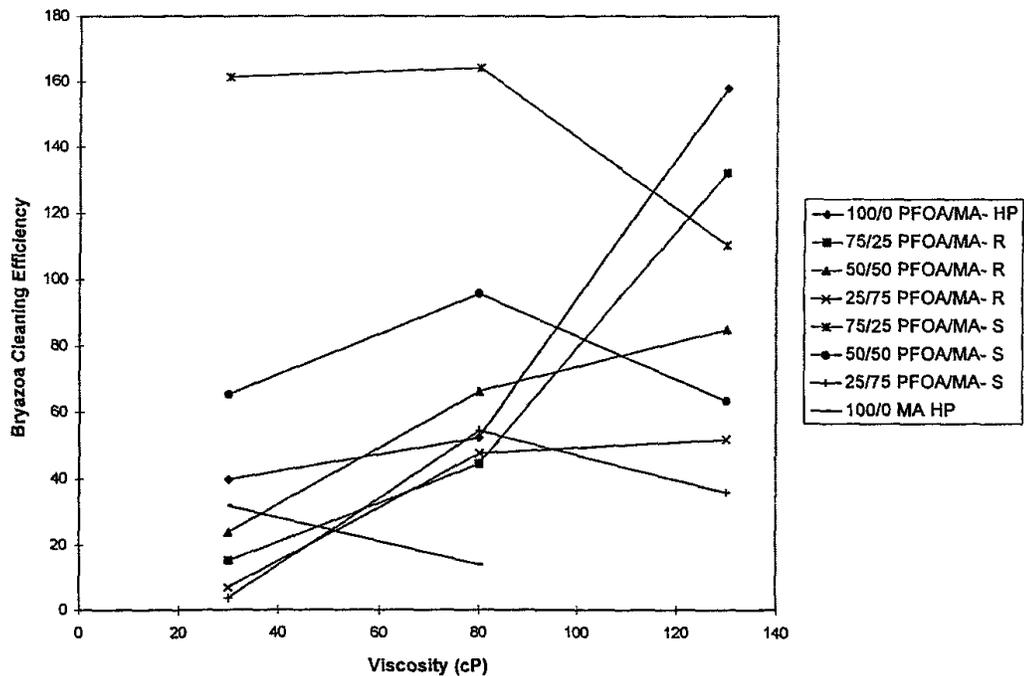


FIGURE 6. Cleaning efficiencies (% relative to control) derived from bryazoa species for HIMW random (R) and segmented (S) copolymer (CP) and homopolymer (HP) coatings prepared from different solution viscosities.

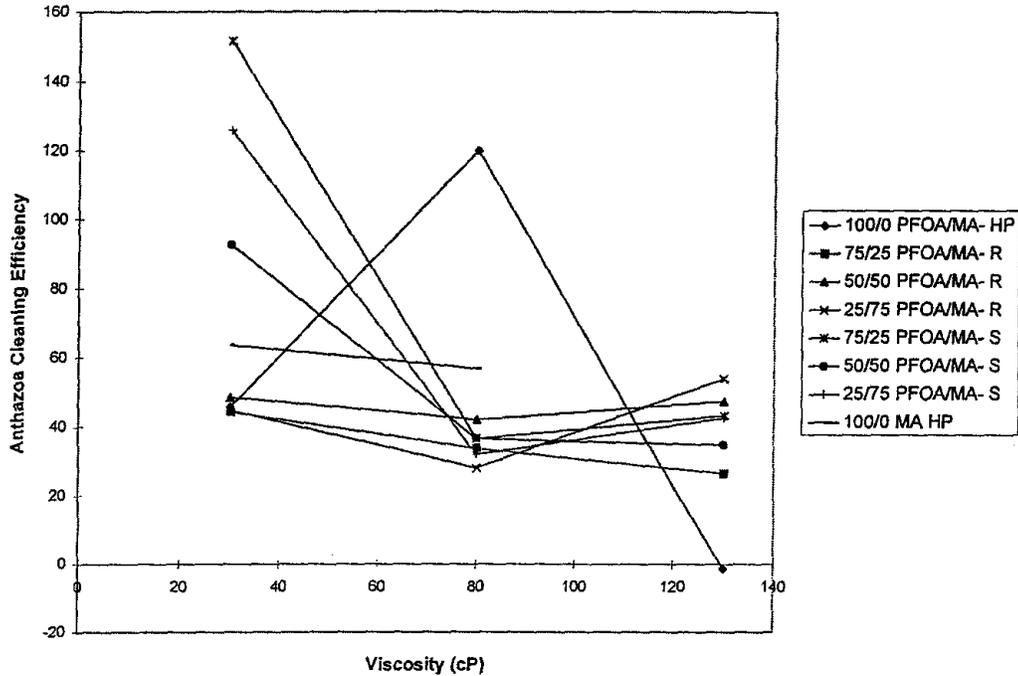


FIGURE 7. Cleaning efficiencies (% relative to control) derived from anthaxia species for HIMW random (R) and segmented (S) copolymer (CP) and homopolymer (HP) coatings prepared from different solution viscosities.

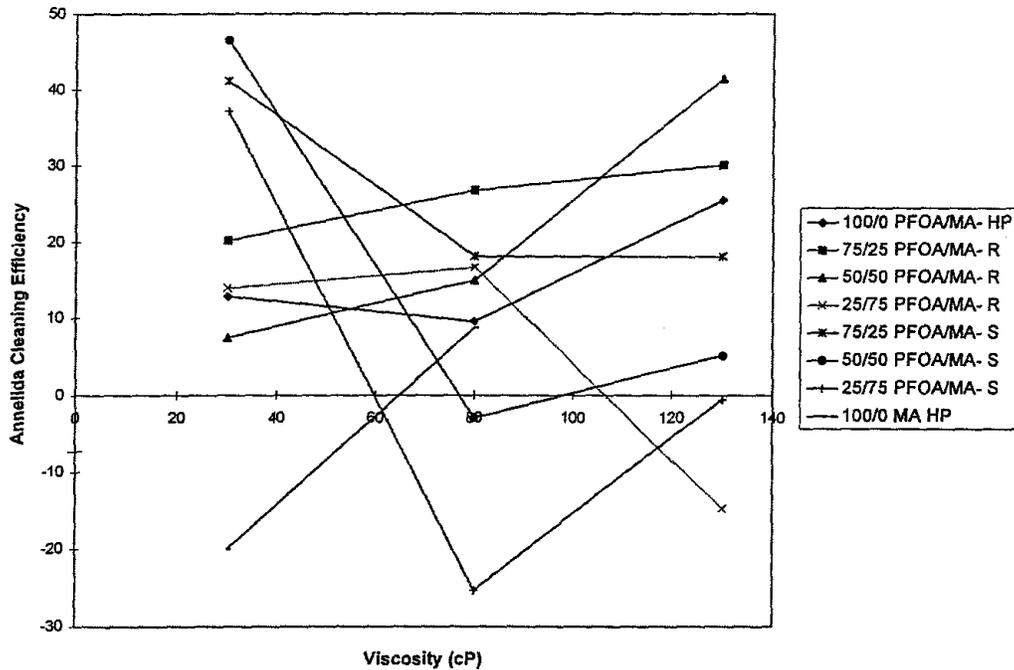


FIGURE 8. Cleaning efficiencies (% relative to control) derived from annelida species for HIMW random (R) and segmented (S) copolymer (CP) and homopolymer (HP) coatings prepared from different solution viscosities.

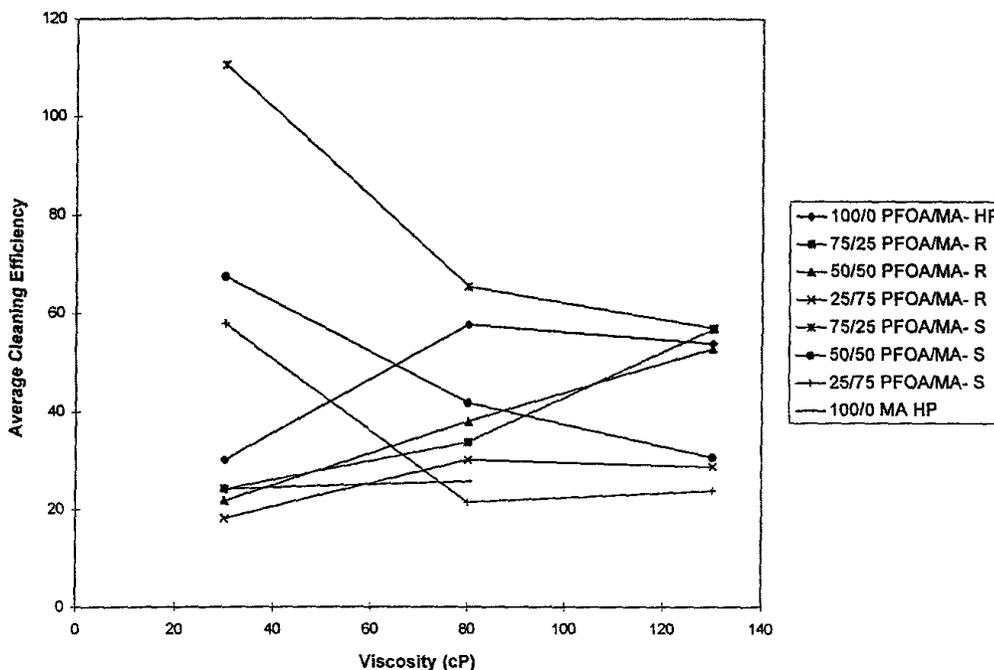


FIGURE 9. Average cleaning efficiencies (% relative to control) derived from individual treatments of species common to all coatings for HIMW random (R) and segmented (S) copolymer (CP) and homopolymer (HP) coatings prepared from different solution viscosities.

SUMMARY AND CONCLUSIONS

New FR coatings have been prepared from new low surface free energy fluoropolymer materials described in a companion paper.¹ These coatings have been sprayed from solution to produce coating surfaces with systematically varied chemical and physical properties. Fouling experiments were performed and cleaning efficiencies determined for these coatings. Our approach has utilized compositional and structural variation, combined with spraying at variable solution viscosities, to produce coatings with experimentally distinct cleaning behaviors. Current efforts are focussed on correlating physico-chemical properties with the degree of fouling and cleaning efficiency. Surface characterization experiments have been designed and are being performed to evaluate what properties, in addition to low surface energy, contribute to the overall fouling release mechanism.

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