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The Settlement of Fouling Organisms on Hydrophobic Surfaces

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December 1977

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THE SETTLEMENT OF FOULING ORGANISMS ON HYDROPHOBIC SURFACES

INTRODUCTION

Two main approaches may be considered in the search for methods to reduce the deleterious effects of biological growth (fouling) on structures and equipment immersed in the sea. On one hand, surfaces may be made toxic, to kill or forestall development of any prospective fouling organism which approaches. Thus far, sufficient fouling resistance has only been found with surfaces that release toxic material into the adjacent seawater, to be ingested by or otherwise repel organisms nearby. Another approach is to determine those properties of surfaces which are not conducive to settlement and attachment by fouling organisms. If generalizations in this regard can be found, surfaces may be designed which optimize fouling resistance. Under some circumstances, both approaches may be used. For example, anti-fouling toxic materials might be so formulated that even when the release of toxic material has declined too much to prevent fouling, subsequent attachment is delayed. In those situations where toxic coatings cannot be applied, the frequency of cleaning may be reduced by proper choices of materials. This report summarizes some recent work concerning the effect of surface properties of immersed materials on the attachment of fouling organisms.

BACKGROUND

In most areas of adhesive technology, the solid surfaces leading to good adhesive joints are found to be well wetted by the materials used as adhesives, and it is difficult to achieve good adhesion when the solids to be joined (adherends) are not easily wettable. In order for good wetting to occur, the critical surface tension of the solid (which is closely related to the surface energy) should be greater than the surface tension of the adhesive (Zisman 1963). Thus, low surface energy materials such as polyolefins or fluorinated plastics are not well wetted by the usual adhesives, are hard to join, and are hydrophobic, i.e. not well wetted by water, a high surface energy liquid.

The usual adhesive practice is to apply the adhesive to adherends which are as free of other contaminating materials as is feasible. In the case of biological adhesion, however, all components of the joint are immersed in an aqueous medium, and some competition between an adhesive and the immersion medium for the adherend surface is possible.

Note: Manuscript submitted November 18, 1977.

Thus, the criteria for wetting, attachment, and adhesion may be modified.

Biological studies of cultured cells, the blood clot, and the blood components involved in clotting, the platelets, show that they adhere best to hydrophilic surfaces which are of high surface energy (Taylor, Baier 1970). This is in general agreement with most adhesive technology. However, in view of the differences between systems of cultured cells and blood components on one hand and marine fouling organisms on the other, some short-term experimental studies of the preference of marine fouling organisms for surfaces of hydrophilic and hydrophobic character have been carried out with the cooperation of several colleagues. The results of the studies are reported here: they show that hydrophobic surfaces may be more supportive of attachment of fouling organisms than hydrophilic surfaces in some instances.

EXPERIMENTAL PROCEDURES AND RESULTS

The organisms studied were a marine bacterium (Pseudomonas sp. NCMB 2021, with Dr. M. Fletcher); a marine alga (Chlorella vulgaris, in the laboratory of Prof. T.R. Tosteson); a bushy fouling bryozoan (Bugula neritina, with J. Mihm); an encrusting bryozoan (Watersipora cucullata); and the populations of marine micro-organisms attaching to samples immersed at various stations along the 1976 Caribbean cruise track of the USNS HAYES (with S. Wajsgras).

The surfaces used were glass, mica, and the plastics polyethylene (PE), polystyrene (PS), poly (ethylene terephthalate) (PET), and poly (tetrafluorethylene) (PTFE). Some samples of polystyrene and poly (ethylene terephthalate) were processed in a radio-frequency induced glow discharge apparatus (Harrick Scientific Corp. Ossining, N.Y.) in residual air. The glass, mica, and processed plastics were hydrophilic surfaces: when wet with water, they drained uniformly so that a stable layer of water was retained unbroken even when interference fringes could be seen in the water layer. The unprocessed plastics, on the other hand, were not well wetted: water on these surfaces did not form a stable thin film, but was unstable and drained rapidly and completely after wetting with water. The treatment of PS and PET by glow discharge is of particular interest since such treatment increased their wettability without change in surface roughness detectable in the scanning electron microscope. Thus, while surface roughness affects settlement (Crisp 1974), comparisons at the same apparent roughness are possible in this work.

Polyethylene (PE), PET and PTFE were commercial films with smooth specular surfaces; PS samples were cut from microbiological petri dishes. A sample of PS commercially processed for cell adhesion by a proprietary process (Falcon Plastics Co.) was also used; this surface was hydrophilic.

The most extensive studies were carried out with Dr. Fletcher using the pseudomonad bacterium. Details may be found elsewhere

(Fletcher & Loeb 1976); the data are summarized in Table 1.

The marine alga Chlorella vulgaris has been studied in Dr. Tosteson's laboratory at the Univ. of Puerto Rico for several years, where assays have been developed to evaluate its adhesion. Attachment to surfaces supplied by NRL was determined there, and are summarized in Table 2. Details of the methods are published elsewhere (Tosteson & Almedovar 1971, 1972).

Bryozoans are macrofouling organisms. Although not as familiar as barnacles, they are a significant nuisance in their own right and also form foci of fouling by other organisms since Watersipora is highly resistant to copper antifoulants (Ryland 1970) (Woods Hole Oceanographic Inst. 1952). Colonies of the bryozoans Bugula neritina and Watersipora cucullata were obtained from the Los Angeles and San Diego area by Pacific Biomarine Inc. and shipped to NRL, where they were maintained for periods of up to 3 weeks in an aquarium using Instant Ocean artificial seawater mixture at 15°C. The colonies were kept in the dark except when larvae were required. They were then induced to release larvae by exposure to light; the phototropic larvae were then captured by pipette and placed in dishes containing various test surfaces in fresh Instant Ocean. After 24 hrs, the numbers settled on the test surfaces were counted. The data so obtained are presented in Table 3.

During the 1976 Caribbean cruise of the USNS HAYES, samples of processed and non-processed polystyrene were immersed in the sea for periods of 2 hrs at a number of stations. Samples were rinsed in seawater filtered through Gelman 0.2 μ m membrane filters, fixed by drying at 60°C, rinsed with distilled water, stained with ammonium oxalate crystal violet, and microorganisms counted by optical microscopy. Ten fields on each sample were counted and a summary of the data is presented in Table 4.

All these organisms exhibited a clear preference for the hydrophobic materials.

DISCUSSION

During the course of this work, Eiben (1976) described studies of another bushy bryozoan, Bowerbankia; his data indicated a strong preference for hydrophobic surfaces by the settling larvae. Several other observations previously reported in the literature may also be interpreted in terms of preference for hydrophobic surfaces by marine organisms. Thus: studies cited by Marshall (1976) indicate several species of bacteria associate themselves with interfaces between aqueous and hydrocarbon or air phases, O'Neill and Wilcox (1971) have reported data which indicated a preference for acrylic plastic over glass by bacteria in the Pacific, and barnacle cyprids settle on plastic surfaces more than on glass (although this has been attributed to surface roughness and alkali leached from glass. (Crisp, 1974 and personal communication)).

Since electrical charge on surfaces and sorption of material from solution are also expected to influence surface interactions, we may not state unequivocally that the hydrophobic nature of the surface is the predominant factor favoring settlement, but we have indications that it might be in a number of important situations. This is perhaps surprising in view of the opposite tendency in most adhesive practice, where low energy hydrophobic materials are difficult to attach; however, the under-water environment raises the possibility that hydrophobic interactions are important. Because the tendency for water to form its hydrogen-bonded network structure is quite strong, hydrophobic materials which are not compatible with the structure tend to be expelled from the aqueous phase and aggregated to reduce their surface area in contact with water. Studies of oil droplets attaching to candidate materials for marine coalescence filters (Kaufman 1976) illustrate this point: oil droplets attached to strongly hydrophobic materials immersed in seawater more than to hydrophilic resins which contain appreciable polar components.

Since organism surfaces may vary widely (Stacey & Barker, 1960) (Sutherland 1972) and both immersed material and organism surfaces may be modified by local conditions (Loeb & Neihof, 1975), similar trends may not hold for all organisms under all conditions (Wallace, Loeb & Wilson, 1972) (Dexter *et al.*, 1975) and the extent to which the preference found with the small number of organisms studied in this work is representative of fouling organisms in general must be explored further. However, the possibility exists that the value of hydrophobic materials as anti-foulants may lie more in their possible ease of cleaning than in their initial resistance to fouling.

Current research is directed to evaluating the influence of other properties, such as surface charge, sorption of materials from seawater and the properties of the fouling organism surface, on attachment and adhesion.

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TABLE 1.

Number of bacteria (*Pseudomonas* NCMB 2021) attached to $100\mu\text{m}^2$ after two hour exposure of various surfaces

Material	Critical Surface tension ^(a)	Stability of water film	Number attached
Poly (tetrafluoroethylene) (i.e. Teflon ^R)	19 <u>dynes</u> cm	unstable	31 ± 4
Polyethylene	31	unstable	34 ± 4
Polystyrene	33	unstable	41 ± 4
Poly (ethylene terphthalate) (i.e. Mylar ^R)	43	unstable	38 ± 4
Falconized ^R (i.e. commercially treated) Polystyrene		stable	5 ± 6
R. F. Plasma-treated Polystyrene		stable	3 ± 5
R. F. Plasma-treated poly (ethylene terphthalate)		stable	2 ± 4
Mica		stable	3 ± 4
Glass (microscope slide)		stable	1 ± 2

(a) from Shafrin, 1967

TABLE 2

Number of Chlorella vulgaris attached to 5 cm² after exposure to cultures for 3 hours

Material	Stability of water film	% increase over glass control
Polystyrene	unstable	57 ± 8
Poly (vinyl fluoride) (i.e. Tedlar ^R)	unstable	198 ± 9
Poly (ethylene terphthalate) (i.e. Mylar ^R)	unstable	156 ± 34
R.F. Plasma-treated Polystyrene	stable	10 ± 14
R.F. Plasma-treated Poly(ethylene terphthalate)	stable	-8 ± 9

TABLE 3

Number of bryozoans attached to 18 cm² after 24 hr exposure

Organism	Material	Number Attached	Ratio
<u>Watersipora</u> <u>cucullata</u>	Polystyrene	3 ± 1	10
	R.F. plasma treated polystyrene	0.3 ± 0.3	
<u>Bugula</u> <u>neritina</u>	Polystyrene	36 ± 6	6
	R.F. plasma treated polystyrene	6 ± 1	
	Poly(ethylene terphthalate)	34 ± 8	11
	R.F. plasma treated poly(ethylene terphthalate)	3 ± 2	

TABLE 4
Microorganism settlement on samples after 2 hr. exposures in the
Caribbean (USNS HAYES, 1976)

<u>Preference of Attaching Organisms</u>	<u>Number of Stations</u>
Hydrophobic	18
Hydrophilic	0
No clear preference	2