Surface Modification Approach to Control Biofouling

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Abstract There are three principal approaches to control biofouling: (1) mechanical detachment of biofoulers if possible; (2) killing or inactivation of biofouling organisms using antibiotics, biocides, cleaning chemicals, etc. and (3) surface modification turning the substrate material into a low-fouling or non-sticking (non-adhesive) one. Such modification usually alters the surface chemical composition and morphology, surface topography and roughness, the hydrophilic/hydrophobic balance, as well as the surface energy and polarity.

In marine applications especially, current non-toxic biofouling control strategies are based mainly on the third approach, i.e., on the idea of creating low-fouling or non-adhesive material surfaces, an approach that includes development of strongly hydrophilic "water-like" bioinert materials. Strongly hydrophobic low-energy surfaces are preferable in industrial and marine biofouling control because of their relative stability in aqueous media and reduced interactions with living cells.

This chapter presents a brief overview of some possibilities for biofouling control by surface engineering. A number of related ideas will be discussed in this chapter, including: (1) the use of protein adsorption as a mediator of bioadhesion and biofouling, (2) physicochemical parameters influencing these phenomena, (3) theoretical aspects of cell/surface interactions, (4) some popular surface modification techniques, and (5) examples of successful biofouling control approaches.

1 Introduction

Biofouling may be defined as any non-desirable accumulation and growth of living matter on material surfaces (see Pasmore 2008). It is a worldwide problem affecting a multitude of industrial water-based processes, including pulp and paper manufacturing,

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food processing and packaging, cooling towers, biomaterials production, membrane technologies, underwater constructions and sensors, ship hulls, fishing farms, heat exchangers, and water desalination systems. The cumulative cost of biofouling due to lost production and only partially successful remedial efforts may run into billions of dollars per year worldwide, which explains the outstanding interest in the development of effective and economical control measures.

There are three principal approaches to solving the biofouling problem: (1) mechanical detachment of biofouling organisms and/or adsorbed biomolecules (i.e., biofoulers and biofoulants, respectively), (2) inactivating or killing the biofilm using antibiotics, biocides, cleaning chemicals, etc., and (3) surface modification with the aim of turning the substrate material into a low- or non-sticking (i.e., non-adhesive) one. Such modification usually alters the surface chemical composition and morphology, surface topography and roughness, the hydrophilic/hydrophobic balance, and the surface energy and polarity. The most effective antifouling coatings available today contain toxic biocides and will therefore be banned by the year 2008 (Brady 2003).

Current non-toxic biofouling control is based mainly on the third approach, i.e., on creation of low-fouling or non-adhesive material surfaces, an approach first applied to the development of bioinert materials where strongly hydrophilic "water-like" surfaces appear more promising. Strongly hydrophobic low-energy surfaces are preferable in industrial and marine biofouling control settings because of their stability in aqueous media and reduced interactions with living cells (Abarzua and Jacubowski 1995).

Biofouling is perceived as a multistage process starting with a "conditioning film" (biofilm) formation in which the adhesion of microfoulers (i.e., bacteria, diatoms, algae, etc.) to the surface is an important step. The industrial and marine biofouling usually continues with settlement of soft and hard macrofoulers such as algae, barnacles, mussels, tubeworms, etc. In principle, it should be possible to prevent or at least reduce biofilm formation by creating material surfaces to which bacteria cannot initially attach. In practice, synthetic materials that are capable of preventing bacterial adsorption are still rather elusive, despite a significant volume of research (Callow and Fletcher 1994).

Surface modification approaches leading to the creation of low-energy, low-adhesive, non-sticking surfaces is accepted nowadays as the most promising ecology-friendly alternative to the use of toxic biocides.

2   Biofouling and Bioadhesion

Upon submersion in a non-sterile aqueous liquid, most surfaces become rapidly colonized by bacteria and other microorganisms. These attached cells and extracellular polymeric substances (EPS), along with extracellular material (e.g., extracellular biopolymers) constitute a biofilm (Costerton et al. 1987). Biofilm frequently forms even on antifouling surfaces containing biocides. According to Brusscher et al. (1995), initial (reversible) bacterial adhesion to a surface is the primary determinant

for biofilm formation. The reversible interactions between a bacterium and a substrate depend on the physicochemical properties of the bacterial cells and substrate surface, as well as the medium. On the other hand, bacteria adhering onto a surface usually secrete a matrix (EPS), in order to cement themselves (irreversible adhesion) to the surface (Van deVivere and Kirchman 1993; see Smeltzer 2008).

The nature of the bioadhesive interactions in the biofouling process is one of the main questions of many current researchers because a fundamental understanding of their molecular mechanisms can guide the creation of material surfaces preventing or reducing biofouling. Several modes of adhesion bonding, such as chemical and electrostatic interactions, mechanical interlocking, diffusion, etc. are currently known (see Smeltzer 2008). The adhesion of microorganisms is very complicated because not just one motif is followed, but rather a combination of modes has been demonstrated. In addition, the types of adhesion mechanisms that are manifested by a biofilm are largely dependent upon the species composition and physiology of the biofilm. The specific surface structures of microorganisms such as pili, cell wall components, and EPS are also known to influence biofilm formation. Finally, bioadhesion and biofouling can be strongly dependent on surface hydrodynamic conditions (Casse and Swain 2006).

Ikada et al. (1984) theoretically predicted that the work of adhesion (i.e., the interfacial surface energy) in aqueous media, $W_{12,w}$, approaches zero when the water contact angle, Q, approaches zero or 90°, i.e., there are two possibilities for a mate-
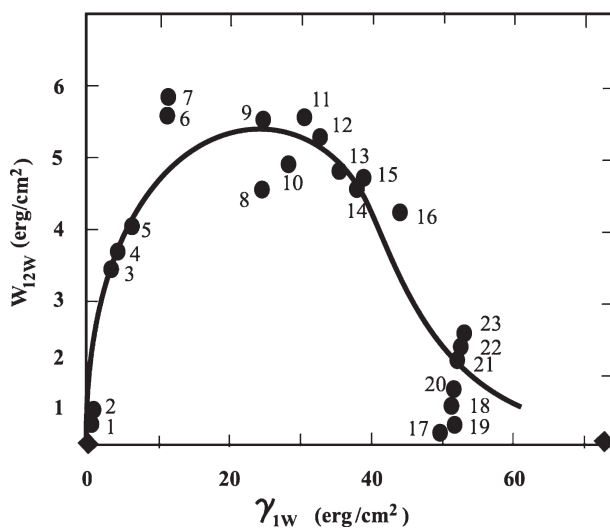

Fig. 1 Work of adsorption of bovine serum albumin (BSA) in water, $W_{12,w}$ against interfacial free energy between water and polymer, γ_{1w}: *1* canine vein; *2* canine artery; *3* poly(vinyl alcohol); *4* cellulose; *5* polyurethane S; *6* polyurethane T; *7* polyurethane E; *8* poly(vinyl chloride); *9* nylon 6,6; *10* poly(methylmethacrylate); *11* poly(ethyleneterephtalate) A; *12* poly(ethy-leneterephtalate B; *13* PVC; *14* nylon 11; *15* poly(styrene); *16* poly-(styrene); *17* poly(trifluoroethylene); *18* paraffin; *19* PTFE; *20* PP; *21* LDPE; *22* MDPE; and *23* HDPE (Ikada et al. 1984)

rial surface to have $W_{12,w}$ approaching zero. In other words, the two possibilities to be non-adhesive are (1) to create a super-hydrophilic, i.e., water-like surface (surface energy, $g_{1w} \sim 0$) and (2) to create a super-hydrophobic surface (see Fig. 1)

This theoretical prediction, experimentally confirmed by BSA adsorption on various polymer surfaces in phosphate buffer, represented a point of departure in the development of strongly hydrophilic or strongly hydrophobic, low-adhesive, protein-repellent, bioinert materials and non-sticking fouling release surfaces.

Many attempts to explain bioadhesion have been made in terms of the thermodynamic theory of Derjaguin, Landau, Verwey and Overbeek (DLVO theory) that explains the stability of lyophobic colloids at solid–liquid interfaces (Derjaguin 1955). In addition to DLVO forces (i.e., Van der Waals and electrostatic), other types of interactions (such as hydrophobic interactions in polar media, ion bridging, and steric interactions) as well as some external cellular appendages are thought to play an important role. The net effect is a balance between all possible interactions (Oliviera 1997.)

Admittedly, such considerations treat the microorganisms as "living colloids," disregarding the specific roles of bacterial structures such as pili and cell wall components that play an important role in bioadhesion at the latter stages of biofilm formation (Morra and Cassinelli 1997). According to a number of authors, these structural features are of less significance in the initial stages of the attachment process than the intrinsic thermodynamic factorsinvolved (Van Loosdrecht et al. 1990; An and Friedman 1998; Morra and Cassinelli 1997). The study of Cunliffe et al. (1999) shows that over the time period of protein adsorption and initial cell attachment (1–24 h), this assumption is reasonable since the overall pattern of cell adhesion to different substrates was similar among the various cell types, although the absolute numbers varied considerably.

A review of bioadhesion-resisting surfaces(Kingshott and Griesser 1999) indicates that, in spite of the very large amount of studies on polyethylene glycol (PEG) coatings, there is still controversy about what exactly the properties and modes of action of an "ideal" PEG coating should be. While some studies have reported no irreversible protein adsorption, other very similar coatings appear less able to resist bioadhesion. Vladkova et al. (1999) found that not only the amount but also the conformation of proteins adsorbed on PEG layers is important for the cellular interactions.

The biofilm protects its habitants from predators, dehydration, biocides, and other environmental extremes while regulating population growth and diversity through primitive cell signals (see Smeltzer 2008). Dunne (2002) has demonstrated that from a physiological standpoint, surface-bound bacteria behave quite differently from their planktonic counterparts.

Recently, some researchers have attempted to replace the relatively crude macroscopic measurements used to describe bacterial adhesion to surfaces (e.g., cell hydrophobicity via contact angle measurements or water–hexadecane partitioning) with methods that directly measure cell-surface interaction forces (repulsive and attractive) using, for example, atomic force microscopy (AFM) to observe homogeneity and topography of bacterial surfaces as well as to directly measure adhesion forces (Velegol and Logan 2004; Li and Logan 2004; Xu and Logan 2005.)

Unfortunately, the mechanisms underlying the adhesion of bacteria to the material surface are still not properly predictable from these theories. Electrostatic and Lifshitz–van der Waals forces are usually considered responsible for the interactions at the biomaterial interface. Studying the role of chemical interactions in bacterial adhesion to polymer surfaces, Speranza et al. (2004) found an important role of the acid/base (Lewis) interaction. Pedry (2005) employed contact angles to relate interfacial free energies between the interacting surfaces. The thermodynamic approach treats the bacteria/substrate interaction as an equilibrium process. This investigation indicates that the more hydrophobic a substrate is, the less of an equilibrium process the interaction becomes. The relationship obtained for the free energy change occurring when bacteria attach to a surface considers only dispersion forces. But, other forces such as electrostatic forces probably also contribute to the interaction and the simple model should include other interactions in order to accurately model bacterial adhesion.

Lately, the concept of the "theta surface" (Baier 2006) has been developed as a contribution to the need predicted by Larry Hench for a robust "general field" theory that supports bioengineering solutions for biocompatibility and biofouling control. For such a theory, there will be no need to know the names or identities of specific biological substances that will be encountered, since all biological systems share the same fundamental chemistry and pattern of events.

A "theta surface" defines the characteristic expression of outermost atomic features least retentive of depositing proteins, and identified by the bioengineering criterion of having measured critical surface tension(CST) between 20 and 30 mN m^{-1}. Material applications requiring strong bioadhesion must avoid this range, whereas those requiring easy release of accumulating biomass should have "theta surface" qualities. More than 30 years of empirical observations of the surface behavior of various materials in biological settings, when correlated with contact angle-determined CST for the same materials, support the definition of the "theta surface". It derives from the concept of "theta solvents" for macromolecules, that is, suspending liquid phases that allow large, complicated molecules such as proteins to retain their thermodynamically most stable conformations, resisting "denaturation" in 3-dimensional suspensions. The theta surface is that atomic force expression controlled from solid surfaces, placed into aqueous biological media, that will least denature glycoproteinaceous macromolecules encountering those surfaces. It is the adsorbed configurations, and strengths of binding/retention of biomass to contacting materials under water, that determine resistance to shear-induced re-entrainment of that matter into the biological stream. So, maintenance at the interface of near-solution-state conformations of the first arriving macromolecules is the most effective approach to thrombus-resistant materials for long-term contact with flowing blood, and to fabrication of "easy-release" coatingsfor exposure to any other biological system (from sea water to dairy products, and from water purification units to sewage flow lines). Universal features of all such systems are the presence of water and glycoproteinaceous macromolecules or their refractory remnants (e.g., surface-active humic substances in the sea) as the dominant "conditioning film," forming water-displacement agents entropically favored as the new interfacial occupants.

Bioadhesion manifests at every stage of biofouling, including the settlement of macrofoulers such as barnacles, mussels, algae, etc. (see Flemming and Greenhalgh 2008; Nedved and Hadfield 2008; Harder 2008). Marine mussels are experts in bonding to a variety of solid surfaces in wet, saline and turbulent environments. The bonding is rapid, permanent, versatile, and protein based. In mussels, adhesive bonding takes the form of a byssus (a bundle of extracorporal threads) each connected to living tissues of the animal at one end and secured by an adhesive plaque at the other. Trying to perform reverse engineering of bioadhesion in marine mussels, Waite (1999) investigated the composition and formation of byssal plaques and threads with the hope of discovering technologically relevant innovations in chemistry and materials science. All proteins isolated from the byssus to date share the quality of containing the amino acid, 3,4-dihydroxyphenylalanine. This residue appears to have a dual functionality, with significant consequences for adsorption and cohesion. On the one hand, it forms a diverse array of weaker molecular interactions such as metal chelates, H-bonds, and pi-cations: these appear to dominate in surface behavior (adsorption). On the other hand, 3,4-dihydroxyphenylalanine and its redox couple, dopaquinone, can mediate formation of covalent cross-links among byssal proteins (cohesion). One of the challenges in making functional biomimetic versions of byssal adhesion is to understand how these two reactivities are balanced.

Flammang and Jangoux (2004) have studied bioadhesion models of marine invertebrates relating to biomechanical, morphological, biochemical, and molecular processes involved in the adhesion. They have found that the adhesion of Cuvenian tubules, which are specialized adhesive defense organs of some sea cucumber species, is instantaneous. The results of this investigation suggest that the underwater adhesive is in the form of a low molecular weight precursor protein in the secretory granules of the adhesive cells. Upon release, these proteins instantly polymerize, with no enzymatic curing required.

Holm et al. (2006) have found inter-specific variation in patterns of adhesion of marine fouling, studying the adhesion of six hard fouling organisms (barnacles, mollusks, and tubeworms) to 12 silicone fouling release surfaces. Removal stress (adhesion strength) varied among the fouling species and among the surfaces. None of the silicone materials generated a minimum in removal stress for all the organisms tested. These results suggest that fouling release materials do not rank (in terms of adhesion strength) identically for all fouling organisms, and thus development of a globally effective hull coating will continue to require testing against a diversity of encrusting species.

3 Physicochemical Parameters Influencing Bioadhesion and Biofouling

Despite the fact that there is no general theory of bioadhesion, a lot of factors influencing bioadhesion and biofouling are now known that could be used in biofouling control. Even though the ability to resist protein, glycoprotein, and polysaccharide adsorption remains imperative for a coating to prevent marine and industrial fouling,

it has been suggested that surface free energy, mechanical properties, and wettability also play an important role in defining the extent to which a surface can resist biofouling and facilitate fouling release (Finlay et al. 2002; Brady and Singler 2000; Sigal et al. 1998).

3.1 Surface Energy and Related Parameters

Leading theories attempt to correlate the kind and intensity of biological responses to surface and interfacial energetics (Brusscher et al. 1995). Surface thermodynamic characteristics, such as hydrophobic/hydrophilic balanceand van der Waals and donor/acceptor forces, are determined by contact anglemeasurements. The surface free energy of the substratum is now accepted as one of the main factors influencing microbial adhesion. Adhesion to surfaces with different surface free energies has been studied by a large number of research groups. For a homogenous solid, the critical surface tension$_c$ is the same as the surface free energy, i.e., surface tension assuming that there are no other forced elastic strains on the solid and no solvent adsorption (Good 1992).

Baier (1973) and Dexter (1979) were among the first researchers to correlate the adhesion of fouling organisms with the surface free energy of the substratum. Hamza et al. (1977) have showed that bacterial adhesion is less on hydrophobic surfaces with a low surface energyand that they are easier to clean because of weaker binding at the interface. McGuire and Swartzel (1987) found an optimum surface free energy, of 30–35 nM m^{-1}, at which milk protein adsorption is minimal. There are also researchers that have drawn the opposite conclusion that hydrophilic membranes have smaller biofouling tendency than hydrophobic ones (Pasmore et al. 2001).

Bacteria adhere to almost any surface, despite continuing arguments about the importance of the physicochemical properties of substratum surfaces, such as hydrophobicity and charge. Bos et al. (2000) demonstrated that bacteria do not have a strong preference for adhesion to hydrophobic or hydrophilic surfaces but that the substratum hydrophobicity is a major determinant of bacterial retention while it hardly influences bacterial adhesion.

Studying the attachment of bacteria, like Salmonella, etc. to different surfaces and the influence of their free energy, Sinde and Carballo (2000) found that the bacterial adherence could not be correlated with surface free energies or contact angles of bacteria.

In the case of soft fouling species (e.g., *Ulva* spores) using non-polar, self-assembled monolayers, it has been shown that adhesion is strongly influenced by critical surface tension (or "wettability") (Finlay et al. 2002).

A generalized relationship between surface tension (i.e., the free energy of a surface, which is commonly referred to as "surface energy") and the relative amount of bioadhesion has been established as shown in Fig. 2. This is commonly known as the "Baier curve" (Anderson et al. 2003). The key feature of this curve is that the minimum in the relative adhesion, at 22–24 nM m^{-1}, (mJ m^{-2}), does not occur at the lowest surface energy.
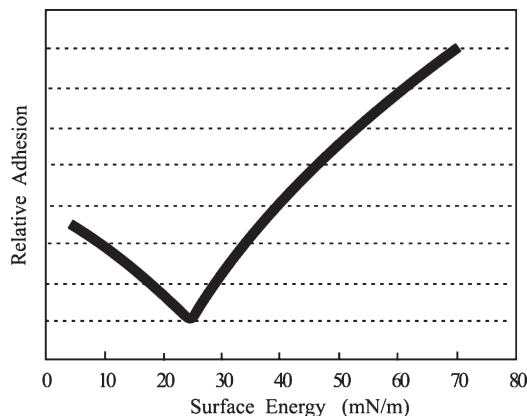
Fig. 2 The "Baier curve" (Anderson et al. 2003)

Recently, Zhao et al. (2004) investigated the effect of surface free energy on bacterial adhesion and reported the optimum surface free energy at which the bacterial adhesion force is minimal to be about 20–30 nM m^{-1}.

Schmidt et al. (2004) studyied adhesive and marine biofouling release properties of coatings containing surface-oriented perfluoroalkyl groups andhave found that the fouling release properties of the low-surface-energy surfaces cannot be evaluated by using only static or advancing contact angle. Contact angle hysteresis appears to be a direct indication of the liquid or adhesive penetration and to correlate with marine biofouling resistance.

Dahlström et al. (2004) have shown that the initial surface wettabilityis of importance in the settlement of macrofouling larvae, such as barnacles, bryozoans and hydroids in both field and laboratory assays. Studying the settlement on surfaces with different wettability, they concluded that the wettability might cause a biological inhibition by interacting with chemo-receptors when the larva is making surface contact, or that the inhibition might be of a physicochemical nature and, thus, surface contact is impeded by repulsive chemical forces.

Holland et al. (2004) have found that fouling release poly(dimethylsiloxane) (PDMS) coatings accumulate diatom slimes, which are not released even from vessels operating at high speeds (>30 knots). Fouling diatoms adhere strongly to a hydrophobic PDMS surface and this feature maybe contributes to their successful colonization of the fouling release coatings.

Studying the effect of substratum surface energy and chemistry on attachment of marine bacteria and algal spores, Ista et al. (2004) and Walker et al. (2005) have found that a number of macroorganisms, such as algae, exploit unicellular forms for attachment and colonization of surfaces. Surface coverage by both macro- and microorganisms depends initially on the ability of single cells to adsorb and adhere to the attachment substratum.

Meyer et al. (2006) have confirmed that silicone coatings with critical surface tension(CST) between 20 and 30 nM m^{-1} more easily release diverse types of

biofouling than materials of higher or lower CST. Oils added to these coatings further selectively diminish the attachment strength of different marine fouling organisms, without significant modification of the initial CST. They have also demonstrated some contact angle anomalies indicating that surface-active eluates from silicone coatings inhibit the adhesive mechanisms of fouling organisms.

3.2 Elastic Modulus

In order to control adhesion of biological organisms to a substrate, some fundamental fracture mechanics have to be considered. For prediction of the force required to break an adhesive from a silicone elastomer substrate, basic fracture mechanics should be examined. Griffith (1921) formulated the following equation for the critical stress (s_c) required to propagating a crack in a plate for a uniaxial direction:

$$\sigma_c = \sqrt{EG_c / \pi a (1 - \upsilon^2)} \tag{1}$$

where E, G_c, a, and υ are the elastic modulus, Griffith's critical fracture energy per area, half the crack length, and Poisson's ratio, respectively. Griffith then applied this equation to the stress over a set crack area ($A = pa^2$), known as the critical pull-off force (P_c): (2)

$$P_c = \sqrt{\pi EG_c a^3 / (1 - \upsilon^2)} \tag{2}$$

A few years later, Kendall (1971, 1994), following Griffith's fracture analysis to model adhesion of elastomer substrates, derived the critical pull-off force for thin elastomer film and radius of the disc being smaller than the size of the elastomer film:

$$P_c = \pi a^2 (2G_c K / t)^{\frac{1}{2}} \tag{3}$$

where: G_c, a, t and K are the critical fracture energy, radius of the contact area, elastomer thin film thickness, and bulk modulus [$K = E/3(1-2)$]. These equations show that there is a proportional relationship between the critical pull-off forceand $(EG_c)^{1/2}$, which are material properties. In this case, fracture energy is directly related to the work of adhesion, which is then equal to the critical surface tension (g_c) of the elastomer (Silberzan et al. 1994; Kendall 1994). As a result, the adhesion correlates with $(Eg_c)^{1/2}$. The elastic modulus and surface energy are parameters that can be engineered with the material.

Thus, from a fracture mechanics study it has been shown that the elastic modulus is a key factor in bioadhesion and the ability of organisms to release from a surface (Brady and Singler 2000; Berglin et al. 2003).

Figure 3 demonstrates that the adhesion correlates better with $(Eg_c)^{1/2}$ than with either surface energy or elastic modulus on their own, despite some scatter in the data.

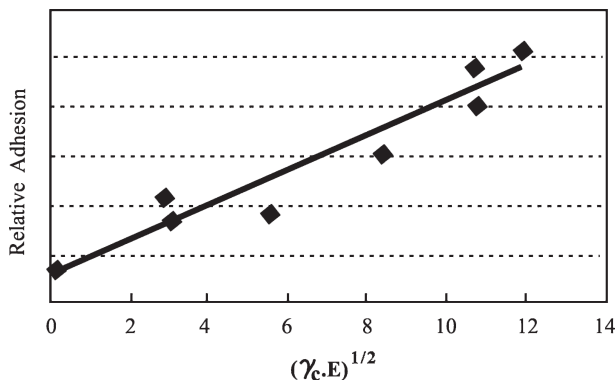**Fig. 3** Relative adhesion as a function of the square root of the product of critical surface free energy (γ_c) and the elastic modulus (E) (Brady and Singler 2000)

For this reason, siloxane elastomers are the major commercial candidates for environmentally benign fouling release coatings, as they possess both low modulus and low surface energy (Wynne et al. 2000). Commercial antifouling silicone elastomers such as RTV11 or Intersleek have modules in the 3–1.4 MPa range (Arce et al. 2003).

3.3 Thickness of Coating

Thickness is another characteristic of low surface energy coatings that plays an important role in bioadhesion (Anderson et al. 2003; Sun et al. 2004). It has been found that below ~100 mm dry film thickness, barnacles can "cut through" to the underlying coats and thus establish firm adhesion. Above this thickness there is no marked improvement in fouling release properties.

Determining the elastic modulus of silicon rubber coatings and films by depth-sensing indentation, Zhili et al. (2004) have observed hard substrate effects when the indentation displacement is less than 10% of the total coating thickness (of 1 mm).

Chaudhury et al. (2005) confirmed the effect of film thickness and modulus on the release of adhered spores and sporelings of the green alga *Ulva*.

3.4 Surface Chemistry

Silicone polymer systems that have generally shown the lowest adhesion of biofoulants are characterized by a specific chemical structure that determines their special behavior and, in particular, their durability and fouling release ability. Siloxane polymers have a backbone of repeating (–Si–O–) units with saturated organic moieties attached to the two non-backbone valences of the silicon. The Si–O bond is

stronger than a C–C bond (451 kJ mol^{-1} compared to 348 kJ mol^{-1}), which helps to explain the long-term durability of these compounds under field conditions. With a length of 1.63 Å, Si–O is longer than the C–C bond in most organic polymers (Baney and Voigt 1977).

This property presents large bond rotation and thus large chain mobility and restructuring ability. As a result, the non-polar and polar groups can reorient on the surface to their most favorable position depending on the environment (Hillborg and Gedde 1999). PDMS) at its lowest energy state is in the all-*trans* conformation due to this arrangement having the most favorable van der Waals interactions where the methyl groups are separated by four bonds (Mark 1979). This ability for recovery to its lowest energy state is beneficial when trying to predict the material properties when exposed to diverse environments.

It has been found that incorporation of low molecular weight silicone polymers (oils) enhances the fouling release properties of PDMS polymers (Milne 1977; Stein, et al. 2003).

Krishnan et al. (2006) studied surfaces of novel block copolymers with amphiphilic side chains for their ability to influence the adhesion of marine organisms. The ability of the amphiphilic surface to undergo an environment-dependent transformation in surface chemistry when in contact with the EPS is a possible reason for its antifouling nature.

3.5 *Slippage*

The fracture mechanic equations assume that the applied force is in the normal direction to the elastomer surface. However, when the force is applied at an angle, as would be the case when a ship is moving, there is the additional component of interfacial slippage that has to be considered. According to Newby et al. (1995), the adhesion of a viscoelastic adhesive on silicone elastomers is controlled heavily by interfacial slippage rather than by thermodynamics. When peeling a viscoelastic adhesive, an extension deformation occurs behind and contraction occurs in front of the moving crack tip (Newby and Chaudhury 1997). If slippage is allowed to occur by the substrate, then the work required to move the crack tip is lowered, which results in a lower adhesion strength. The more mobile chains are on the substrate surface, the lower the friction observed. When force is applied in the normal direction, the release mode is peeling from nucleated voids within the contact area, but when force is directed at an angle, failure occurs by a fingering process (like webbed fingers) as described by Newby et al. (1995) that starts at the edges and moves inward (Kohl and Singler 1999). These finger adhesion release deformations were also shown to increase in length (i.e., amplitude) slightly as the modulus or the thickness of the elastomer coating increased, and significantly as the rigidity of the adhesive increased (Ghatak et al. 2000).

Friction/lubricity is a factor of biological adhesion. In order to engineer the elastomer matrix with lubricity, various non-functional silicone oil additives have been introduced into the bulk of the elastomer. Due to surface energetics, the lower surface

energy silicone oils migrate on the surface creating a lubricious layer (Homma et al. 1999). Oils by their nature are lubricants but this is not the main reason for their efficiency. This is thought to be due to the surface tension and hydrophobicity changes that the oils affect during the curing process and after immersion. It has been shown that fouling release coatings do not rely on leaching of the oils for their fouling release properties. Both laboratory studies (Truby et al. 2000) and ships' trials have shown that performance was maintained for up to 10 years in service (Anderson et al. 2003).

3.6 *Surface Roughness and Topography*

In addition to surface free energy, elastic modulus, and surface chemistry, other factors, including surface roughness and topography, also significantly influence bacterial adhesion. Therefore the mechanism is very complex. Surface roughness influences the spreading of liquid cements secreted by organisms to increase adhesion on engineered topography. With the fracture mechanisms discussed previously, the surfaces were assumed to be completely smooth. However, even the smoothest substrate has molecular roughness on the surface. Depending on the viscosity of the liquid, the adhesive might not fill all the small crevices (Baier et al. 1968). When solidification of the adhesive occurs, there are stress concentrations that occur at the focal points of the roughness. The stress at these focal points is much higher than the applied force, so less applied force is needed to fracture the adhesion. If the voids are relatively close together then the fracture crack can propagate even more easily. The unfilled crevices can be on the molecular level or micron scale depending on the size of the organism.

The trends observed from many studies are that as the roughness increased, the advancing angle increased and the receding angle decreased. This means that when static conditions are examined, as the roughness increases, the contact angle increases and thus the critical surface tension calculated increases. However, this statement does not consider the size, shape, and the exact location of the droplet edge in reference to the rough features, but this roughness influences the spreading of liquid adhesives. Many reports on the cellular responses to topographical cues on both the nanometer and micrometer scales have appeared in the past few decades. However, it has been argued by a number of authors that these structural features are of less significance in the initial stages of the attachment process than the intrinsic thermodynamic factors involved (An and Friedman 1998; Morra and Cassinelli 1997), and a number of detailed studies have been carried out to support this assertion (Van Loosdrecht et al. 1990).

In the area of marine fouling, topography has been shown to alter settlement of bacteria(Scheuerman et al. 1998), barnacles(Berntsson et al. 2000; Berntsson 2001; Berntsson and Jonsson 2003) and algae(Callow et al. 2002; Hoipkemeier-Wilson et al. 2004) and to deter colonization of invertebrate shells(Scardino et al. 2003; Bers and Wahl 2004). The change in wettability of a surfacethat results from surface roughness, i.e., topography, is likely to be contributing factor to these responses.

Prior to adhesion, the swimming zoospore is able to select suitable surfaces on the basis of surface characteristics, such as topography, or on the basis of physico-chemical properties, such as contact angle (Callow et al. 1997, 2000, see Nedved and Hadfield 2008).

Promising antifouling properties of microstructured surfaces have been reported by Bohringer (2003) and Bers and Wahl (2004). Hoipkemeier-Wilson et al. (2004) have studied the settlement and release of *Ulva* spores from microengineered topographies.

Influence of nanoscale topography (Griesser et al. 2002) on hydrophobicity (the contact angles and their hysteresis), including that of fluoro-based polymer thin films (Gerbig et al. 2005), is reported in the special literature. Brennan et al. (2005) have patented surface topography for non-toxic bioadhesion control.

Carman et al. (2006) have experimentally demonstrated the importance of wettability models in predicting cellular contact guidance for engineered topographies, but do not fully explain the process. Bioadhesion is a complex and specific process. The material modulus and surface elasticity of cell membranes are other factors to consider, in addition to the variety of adhesive proteins, glycoproteins, and polysaccharides that organisms secrete. The wettability models are limited by the assumption that the liquid droplet is much larger than the topographical features. This allows for line tension effects to be neglected. Measurements with smaller drop sizes are believed to enable the inclusion of line tension effects. Ultimately, the goal is to improve the predictive quality of an energy-driven model for bioadhesion.

4 Physicochemical Parameters Influencing the Cell/ Material Surface Interaction

The ability of cells to adhere to each other or to the underlying substrate (called cell adhesion) is their main property. Biological adhesion is not fully explained by physical adhesion but is a much more general and complicated phenomenon determined by a number of interacting biological processes such as cell attachment and mobility, cell growth and differentiation, etc. (Bitton and Marshall 1980; Adams and Watts 1993).

Analyzing the special literature and studying experimentally the adhesion interaction of living cells with different model surfaces, Altankov (2003) has concluded that the initial interaction of cells with biomaterials is governed by the efficiency of the cell adhesion, the latter depending mainly on the surface properties of the substrate and the adsorbed proteins. Hydrophilic surfaces support cell adhesion and proliferation, cell growth, and the organization of the focal adhesion complex delivering the signal via integrin receptors. An optimum interaction with cells usually appears at moderate hydrophilicity (WCA ~ 60°). The chemical functional groups oppress it in the following manner:

$-NH_2 > -OH >$ epoxy $> -SO_3 > -COOH > -CF_3$
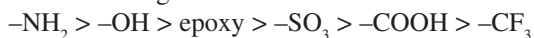
A relationship between the efficiency of the cell interaction and the total negative charge of the surface exists. This interaction is influenced not only by the chemically

grafted functional groups but also by the adsorbed ions. The synthesis and organization of the fibronectin matrix by cells is better on surfaces that weakly bond fibronectin compared to other matrix proteins. The conformation of the adsorbed adhesive proteins also plays an important role in the adhesive interaction of strongly hydrophilic non-charged PEG surfaces (Vladkova et al. 1999).

Properties of the substrate, such as hydrophobicity (Schackenraad et al. 1992), hydrophilicity (Gölander 1986), steric hindrance (Kuhl et al. 1994), roughness (Kiaie et al. 1995), and the existence of a "conditioning layer" at the surface (Abarzua and Jacubowski 1995), are all thought to be important in the initial cell attachment process.

5   Protein Adsorptionas Mediator of Bioadhesion and Biofouling

Protein adsorption is the primary event in biofouling and in the interaction of foreign surfaces with tissue, blood, and cells (Corpe 1970). The biological cascade of industrial and marine biofouling as well as of all undesirable response reactions against biomaterials begins with deposition of proteins. Therefore, low protein adsorption is accepted now as the most important prerequisite for resistance against biofouling.
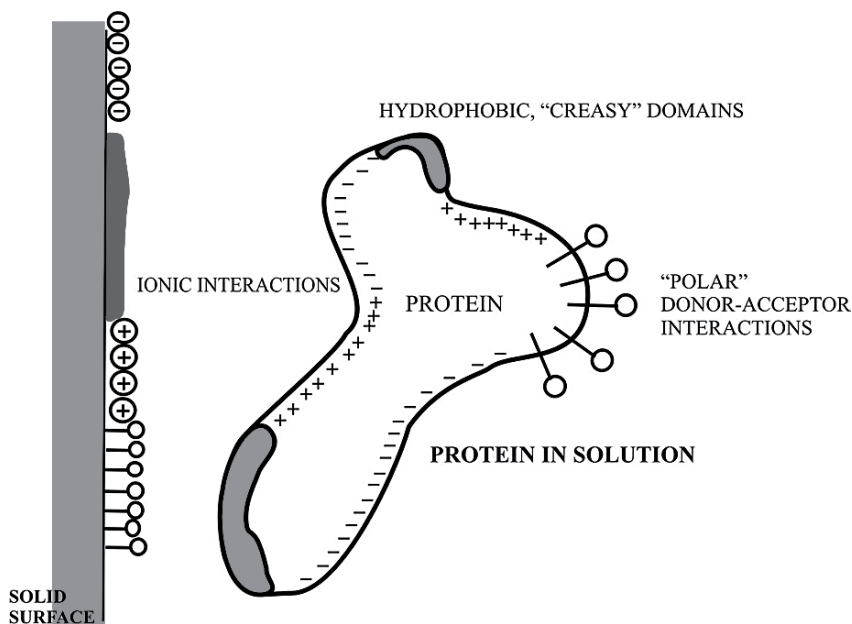

Fig. 4 The versatile nature of proteins (Hlady et al. 1985)

Because of their versatile nature (Fig. 4), different proteins can be adsorbed by various mechanisms when presented with a complementary surface, which makes the prevention of protein adsorption difficult.

Most investigations are devoted to the study of the adsorption of single well-defined proteins, adsorption from multicomponent systems, or from blood plasma and are aimed at identification of protein-repellent biomaterial surfaces (Gölander et al. 1986; Gölander 1986; Malmsten 1998; Pasche 2004; Atthoff 2006).

It is known that the protein adsorption and biocontact properties of polymers depend on surface chemical composition and topography, surface hydrophilic/hydrophobic balance and charge, the mobility of the surface functional groups, the thickness and density of the modifying layer and its adhesion to the substrate, etc. Hence, by changing some of these parameters we can control protein adsorption (Gölander 1986).

According to Loeb and Neihof (1975), and Baier (1980) the adsorption of organic molecules leads to formation of a "conditioning film" on a newly immersed surface, altering the physicochemical properties of this surface and providing a nutrient source for attachment of microbial flora. The primary mechanism in the attachment of marine organisms to surfaces involves secretion of protein or glyco-protein adhesives (Vreeland et al. 1998; Kamino et al. 2000; Stanley et al. 1999). Therefore, it is no surprise that significant attention has been directed toward development of efficient protein-resistant surfaces (Hester et al. 2002; Griesser et al. 2002; Ostuni et al. 2001, 2003; Bohringer 2003; Groll et al. 2004) for marine anti-fouling (Youngblood et al. 2003) as well as for biomedical applications (Gölander et al. 1984, 1986; Wagner et al. 2004; Vladkova 1995, 2001).

Identification of the type and amount of proteins adsorbing to the material surface could provide important information for the rational development of new materials that can resist biofouling. Adsorption of different organisms by adhesive proteins undergoing subsequent underwater curing is thought to be a mediator of bioadhesion and biofouling. Some recent investigations have focused on further study of the curing mechanisms of bioadhesive proteins as well as on the mechanical properties of bioadhesives such as spore adhesive glycoprotein of the green alga *Ulva* (Humphrey et al. 2005; Walker et al. 2005).

Using biomolecules and green alga as probes, comparative evaluations have been performed of the antifouling and fouling release properties of hyperbranched fluoropolymer (HBFP)–poly(ethylene glycol) (PEG) composite coatings and PDMS elastomers. The maximum resistance to protein, lipopolysaccharide, and *Ulva* zoospore adhesion, as well as the best zoospore- and sporling-release properties have been recorded for the HBFP–PEG coating containing 45%wt PEG. This material also exhibited better performance than did a standard PDMS coating (Gudipati et al. 2005).

It is expected that new analytical techniques and direct measurement of interfacial forces between proteins and surfaces will improve understanding of protein/surface interactions and open new possibilities for the guided design of surfaces intended to resist bioadhesion.

6 Protein Repellent Surfaces

6.1 Strongly Hydrophilic Surfaces

Many strongly hydrophilic and hydrophobic surfaces have been developed to decrease protein adsorption to biomaterials (Elbert and Hubbel 1996). A comparative protein adsorption study of different strongly hydrophilic surfaces, including positively charged (*N*-vinylpyrolidon), negatively charged (AA), and non-charged (PEG) have clearly demonstrated the advantages of non-charged strongly hydrophilic surfaces (Gölander et al.,1986).

PEGs, which currently represent the "gold standard" of biomaterials, are most often used in the creation of bioinert material surfaces. The bioinertness of PEG molecules is utilized also in the prevention of marine biofouling using water-resistant hybrid co-polymer networks containing PEG segments. Much research is devoted to study of the protein adsorption resistance mechanisms of different PEG-coated surfaces, for example surfaces with adsorbed PEG-graft copolymers (Pasche 2004).

The structural similarity of the $-CH_2CH_2O-$ unit to water and the strong hydrogen bonding to the O-atom have been used to rationalize its miscibility with water. The $-CH_2-$ groups are believed to be "caged" by a water network (Bailey and Koleske 1976), see Fig. 5. Hence, when a foreign moiety approaches a PEG-coated surface, that moiety behaves as if it was interacting with a hydrated surface and its adsorption is minimized.
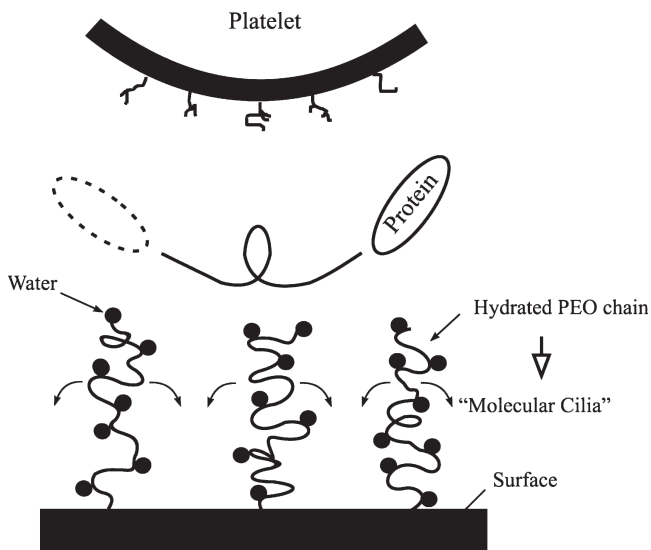

Fig. 5 "Molecular cilia" mechanism on PEG surface with hydrated poly(oxyethylene) chain (Mori and Nagaoka 1982)

PEG-hydrogel

Grafted PEG

Adsorbed PEG
block-copolymer

PEO segment   Cross-linking or   PPO or other
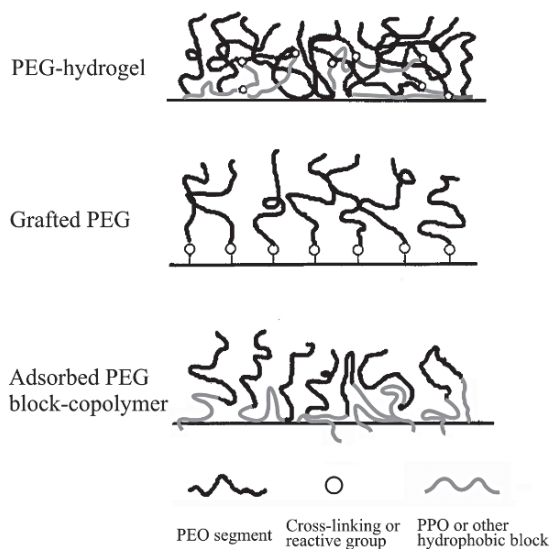   reactive group   hydrophobic block

Fig. 6 Scheme showing the structural features of PEG layers obtained by different coating

A number of experimental techniques have been used to introduce PEG groups on different polymer surfaces, such as PE, PVC, PMMA, NR, PDMS, PS, etc., by wet chemistry or by plasma treatment (Vladkova 1995, 2001; Vladkova et al. 1999; Harris 1992). Wet chemistry methods include deposition of photopolymer hydrogel PEG coatings, including a two-step photopolymerization procedure to increase the surface density of PEG chains (Gölander et al. 1984), grafting, or adsorption of PEG chains on the substrate surface. Structural features of the PEG layers obtained in this way are presented schematically in Fig. 6. Concentrating PEG chains through creation of brush-type surface coatings using mono-functional PEG-acrylates and UV polymerization has been used to prepare super-hydrophilic (water contact angle <10°) surfaces with exclusively low (below 0.05 mg m^{-2}) protein adsorption (Gölander et al. 1984)

PEG-aldehyde (Gölander et al. 1987) and PEG-epoxide grafting or PEG-epoxide/PEI copolymer (Fig. 7) quasi-irreversible adsorption (Vladkova et al. 1999) at optimal reaction conditions also leads to the formation of surfaces with very low protein adsorption of below 0.05 mg m^{-2} (by ellipsometry). Figure 8 shows a simple sketch of PEG-aldehyde grafting by Schiff base reaction with surface NH$_2$ groups.

The examples of PEG-coated surfaces described herein are only a small part of those described in the special literature.

The bioinertness of PEG molecules is utilized in marine biofouling prevention using water-resistant hybrid co-polymer networks containing PEG segments, oriented toward the water in aqueous media (Gudipati et al. 2004, 2005). Surface-responsive materialsfor non-stick coatings are prepared by linking perfluoropolyether (hexafluoro-propylene oxide oligomer, PFPE), poly(dimethylsiloxane) (PDMS)
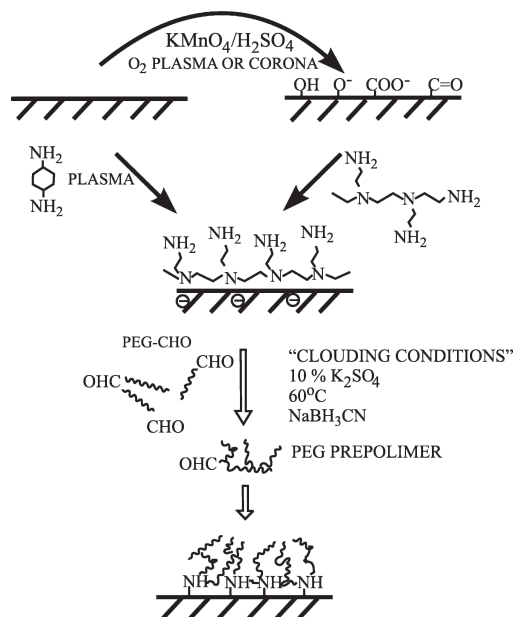
Fig. 7 Grafting of PEG by Schiff base reaction between PEG-CHO and surface-NH_2

and PEG segments. Non-stick properties exhibited in air are due to the presence of PDMS and PFPE at the air–solid interface. Upon exposure to water, this material becomes non-stick due to migration of PEG segments to the water–solid interface Russell (2002).

6.2   Protein-Repellent Plasma Films

Plasma treatment in vacuum or at normal pressure, in atmospheres of different gases, as well as ion- or electron beam, etc., are referred to as "dry" chemistry methods, and they represent another approach to surface modification aimed at creation of easily cleaned or non-fouling material surfaces (Ratner et al. 1990; Chan 1993; Sheu et al. 1995; Chan et al. 1996; Vladkova 2001). Comparative studies of plasma-deposited films indicated that both strongly hydrophobic silicon and strongly hydrophilic PEG surfaces result in very low protein adsorption, unusually weak complement system activation, and low cell and platelet adhesion (Kicheva et al. 1992; Vladkova 1995), which is in agreement with the prediction of Ikada et al. (1984). Similar "dry" chemistry also offers a possibility to turn the hydrophobic surfaces into hydrophilic surfaces and the opposite, to combine the stability of the hydrophobic materials in water with the advantages of the hydrophilic surfaces. For example, PDMS surface modification has been performed to alter the hydrophilic–hydrophobic balance on the surface and hence the interaction with living cells (Satriano et al. 2001, 2002; Vladkova et al.
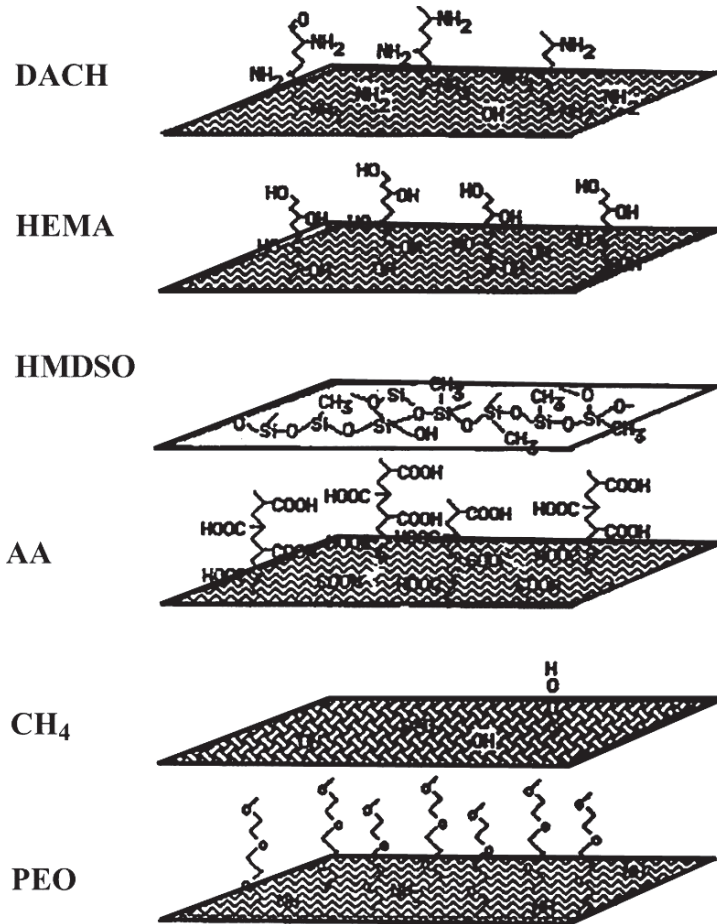
Fig. 8 Chemical composition of plasma-deposited polymer films: diaminocyclohexane (*DACH*), hydroxiethylmetacrylate (*HEMA*), hexamethyldisiloxane (*HMDS*), poly(ethylene oxide) (*PEO*)

2005). Radio frequency plasma discharge is considered as an important technique in the creation of protein-repellent surfaces.

7 Low Surface Energy Coatings to Control Biofouling

Considerable attention in recent decades has been focused on the concept for the creation of non-biocidal, non-toxic coating systems that prevent the attachment of fouling organisms. The objective for these minimally adhesive "fouling release" coatings was to create surfaces reducing the adhesion strength of attaching organisms and hence causing their detachment under their own weight as they grow or

their dislodgement by water movement when a ship moves through the water (Linder 1992). The initial interest in the development of such types of coatings was focused on the fluoropolymers, but later it moved to the siloxane elastomers and their copolymers because of the combination of lower elastic modulus with low surface energy.

The most minimally adhesive polymer surfaces known currently are prepared from siloxanes (Swain and Schultz 1996; Pike et al. 1996; Kohl and Singler 1999; Uilk et al. 2002), fluoropolymers (Schmidt et al. 1994; Wang et al. 1997; Brady et al. 1999; Bunyard et al. 1999; Gan et al. 2003; Gudipati et al. 2004), and fluorosiloxanes (Johnston et al. 1999; Mera et al. 1999; Uilk et al. 2002; Grunlan et al. 2004). Their non-adhesive nature is attributed to low surface energy g, low storage modulus G, and low glass-transition temperature T_g (Owen 1990; Newby et al. 1995; Brady 1999, 2000; Wynne et al. 2000). Low g values reduce polar and hydrogen-bonding interactions with the marine organism's adhesive, thereby decreasing the joint strength. G is also significant because the rupture of an adhesive bond involves viscoelastic flow at the coating surface (Kinloch and Young 1983).

Hybrid xerogel films have also been studied as novel coatings for antifouling and fouling release (Tang et al. 2005). They were found to inhibit settlement of zoospores of the marine fouling alga *Ulva*, hyperbranched fluoropolymer poly(ethylene oxide)

Hyperbranched fluoropolymer–poly(ethylene glycol) (HBFP–PEG) composite coatings have been identified as material exhibiting better antifouling and fouling release performance than standard PDMS coatings (Gudipati et al. 2005).

Minimally adhesive polymer surfaces (MAPSs) from star oligosiloxanes, star oligofluorosiloxanes, and α,ω-bis(3-aminopropyl) PDMS have been prepared by Grunlan et al. (2006). It was found that varying of the molecular weight of the star oligosiloxanes and star oligofluorosiloxanes, as well as altering the ratio to α,ω-bis(3-aminopropyl) PDMS, may enhance their fouling release behavior. Minimally adhesive, fouling release applications of surface-enriched perfluoropolyether (PFPE) graft terpolymer-based coatings are also in the research focus.

Silicone fouling release coatings, facilitating only weak adhesion of macrofouling organisms such as barnacles, tubeworms, and macroalgae (Kavanagh et al. 2003; Stein et al. 2003; Sun et al. 2004) currently represent the only viable commercial alternative to biocide antifouling coatings.

Milne (1977a,b) was among the first researchers who pointed out the antifouling properties of silicone polymers and also observed that the low molecular weight silicone polymers (oils) greatly enhanced their fouling release properties. These early observations constitute the basis of most silicone fouling release systems commercially available today. Intersleek (International Coatings) was the first commercial fouling release coating and its manufacturers recently celebrated the covering of their 100th ship. Hempasil (Hempel Company), EP 2000 and SN-1 HP (E Paint Company), Eco-speed (Chugoku Marine Paints), Phase Coat URF, Si-Coat 560 and 561, etc. are other practically applicable low-surface-energy coatings. However, none of them meet all of the desired performance characteristics.

The use of silicone fouling release coatingsis restricted to larger faster moving vessels. Many lack the toughness to withstand the rigorous physical demands of the

marine environment, do not sufficiently self-clean or, due to polymer restructuring or other degradation pathways, lose many of the desirable surface properties with time and exposure to the marine environment. Therefore, many research groups are looking for new possibilities for solving these problems. For example, the largest research project, which includes 31 organizations across Europe (AMBIO 2006), aims to develop new types of nanostructured fouling-prevention polymeric surface coatings that mimic natural non-fouling surfaces (e.g., dolphin skin, lotus leaf effect).

More recently, Vladkova et al. (2006) succeeded in developing hard fouling-preventing silicone coatings based on industrially produced room temperature vulcanized (RTV) PDMS. Figure 9 demonstrates the biofouling of such sample coatings after 1-year exposure in the Indian Ocean (at the Fishing Harbour, Chennai) where the water salinity, temperature, and concentration of fouling organisms are very high and thus the biofouling is very heavy. No macrofouling, only slime formed mainly by brown diatoms, is observed on these samples exposed in static conditions. Engineered coatings such as these that disallow development of macrofouling under static conditions are suitable for macrofouling prevention of the hulls of slowly moving ships and static underwater constructions.
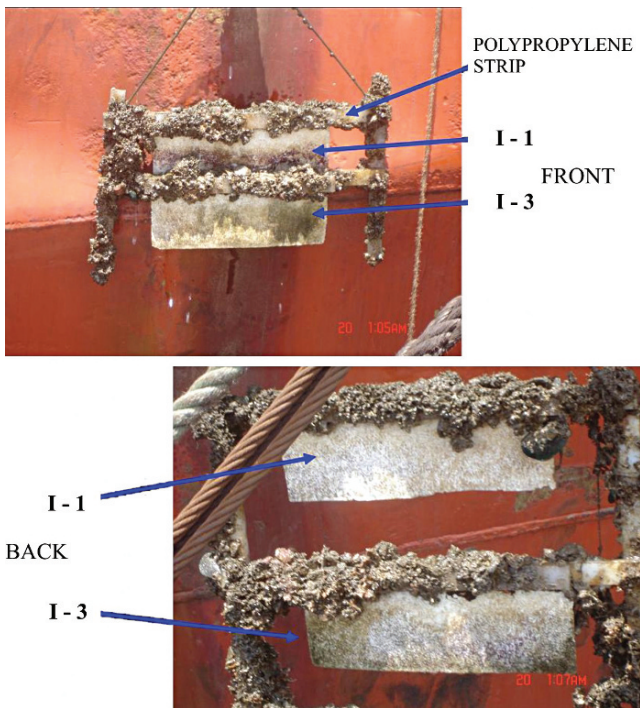

Fig. 9 Fouling of silicone samples after 1-year exposure in the Indian Ocean, Chennai Fishing Harbour

8 Conclusions

A general theory of bioadhesion remains illusive and the molecular details underlying the adhesion mechanisms of fouling organisms remain unclear.

Many physicochemical factors influencing bioadhesion and biofouling are unknown or remain nebulous, such as surface free energy and related parameters, water contact angle and contact angle hysteresis, elastic modulus, surface chemistry, surface roughness and topography, and biological response, etc. Creation of a "theta-surface" represents a new and fundamental antifouling concept, but it is still at the initial step of development.

Surface patterningseems to be a very promising anti-biofouling strategy but from a practical standpoint significant questions remain, such as ablation by water, abrasion by sand particles, etc., under actual field applications. Recently developed polymeric materials that resist such aggressive environmental impacts may eventually make surface-patterning approaches pragmatic, but currently they are too expensive to be commercially viable alternatives.

The creation of exceedingly smooth surfacesmay be a more realistic approach to decreased biofouling. Manipulating the surface topography to enhance smoothness and engineering local surface hydrodynamics should contribute to this approach.

The known fouling release coatings decrease the adhesion strength of the fouling organisms but no one surface is known to prevent the formation of biofilm.

In depth study of the adsorption of adhesive proteins secreted by fouling organisms may be the key to identification of a "universal" surface that would release all biological fouling systems, since the biological cascade of biofouling begins with deposition of such proteins. Surface modification to create material surfaces with suitable composition and morphology would be necessary to control biofouling.

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