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DEVELOPMENT AND EVALUATION OF MODIFIED DLC COATINGS TO MINIMIZE PSEUDOMONAS FLUORESCENS ADHESION

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ABSTRACT

Si and N-doped DLC coatings with various Si and N contents were prepared using a magnetron sputter ionplating technology. The antifouling property of DLC coatings was evaluated with Pseudomonas fluorescens which is one of the most common bacteria forming biofilms on the surface of heat exchangers in cooling water systems. The experimental results showed that bacterial removal by a standardised washing procedure increased significantly with increasing electron donor γ_s^- values and with decreasing electron acceptor γ_s^+ values of DLC coatings. The incorporation of 2%N into the Si-doped DLC coatings further significantly reduced bacterial attachment and significantly increased bacterial removal. The best Si-Ndoped DLC coatings reduced bacterial attachment by 58% and increased removal by 41%, compared with a standard silicone coating, Silastic®T2. Bacterial adhesion strength on the DLC coatings is explained in terms of thermodynamic work of adhesion.

INTRODUCTION

The rapid development of the global offshore industry and of amphibious chemical, steel and power plants has lead to more intensive use of water as a cooling medium. However, heat exchangers and pipelines using water as a coolant suffer from biological fouling in the form of biofilm (Koh *et al.* 1991; Lucas *et al.* 1996). Biofouling not only reduces the heat transfer performance significantly, it also causes a considerable pressure drop, calling for higher pumping requirements. An effective approach to reduce biofouling is to alter the surface properties of the equipment and to make it less attractive for the establishment of microorganisms, so that they can be removed easily from the surfaces by flowing water.

Silicone coatings based on polydimethylsiloxane are being investigated as fouling-release coatings for various applications including ship hulls (eg Kim et al. 2007; Beigbeder et al. 2008). However, the poor thermal conductivity, poor abrasion resistance and poor adhesion to metal substrates of silicone elastomers currently inhibit their commercial use in heat exchangers (Müller-Steinhagen and Zhao 1997). Diamond-like carbon (DLC) coatings have attracted great interest due to their excellent properties such as excellent thermal conductivity similar to metals, low friction, extremely smooth surface, hardness, wear resistance and corrosion resistance (Grill, 1993). DLC is also an excellent base coating to be alloyed with different elements. The amorphous nature of DLC opens the possibility of introducing additional elements, such as Si, F, N, O and their combinations, into the coating whilst still maintaining the amorphous phase of the coating (Hauert 2003). Zhao et al. (2007a) recently explored initial bacterial attachment on silicon-doped DLC coatings, but there are no studies that explore bacterial removal properties from such coatings. In the present study, a range of silicon- and nitrogen-doped DLC coatings with different Si and N contents was produced in order to investigate microbial attachment and release properties of the coatings. The strength of attachment of cells, for a number of applications where the control of biological fouling is critical eg heat exchangers, pipelines, and filtration membranes. The range of surfaces produced was evaluated for attachment and adhesion of Pseudomonas fluorescens, which is one of the most common bacteria that forms biofilms on the surface of heat exchangers in freshwater cooling water systems (Bott 2001).

MATERIALS AND METHODS

Preparation of Si and N-doped DLC coatings

Si-doped DLC coatings were prepared at Teer Coatings Ltd, using their patented unbalanced magnetron sputter ionplating system combined with plasma-enhanced chemical vapour deposition (PECVD). The plates (76 x 26 x 1.2 mm), were precoated with 0.5 μ m CrNi as sublayer. A silicon layer was deposited by pulsed direct current (DC) magnetron sputtering using argon as the working gas, followed by a silicon carbide layer by the addition of butane and sputtered carbon. Finally, a Si doped DLC layer was deposited using a pulsed DC bias and an electrode with a 13.56-MHz radio frequency (RF) generator. The substrates are biased using pulsed DC rather than conventional RF. Both carbon target and butane are used as the carbon sources during the deposition. The Si content in the DLC coatings was altered by changing the sputtering current on the Si target. Three Si-doped DLC coatings with Si contents of 1%, 2% and 3.8% were prepared. The thickness of Sidoped diamond-like carbon coatings was 1 µm. Si-N-doped DLC coatings were prepared by radio frequency (13.56 MHz) PECVD using a mixture of C_2H_2 , Si(CH₃)₄ and N₂ as precursors. Four Si-N-doped DLC coatings with 0.5%Si:2.2%N; 3.7%Si:2.1%N; 9%Si:2.3%N and 20%Si:2%N were prepared. The coatings compositions are given by atomic percentages.

Characterisation of Si and N-doped DLC coatings

Contact angles of coatings were obtained using a sessile drop method with a Dataphysics OCA-20 contact analyser as detailed in Zhao et al. (2007b). Three test liquids were used as probes for surface free energy calculations: water, diiodomethane (Sigma-Aldrich) and ethylene glycol (Sigma-Aldrich). van Oss et al (1998) and Good (1992) presented data for the surface tension components of the test liquids. Surface energies of the coatings and their dispersive and polar components were calculated using the van Oss acid–base (AB) approach (van Oss 1994). The contact angles and derived values for the surface energy of lawns of the bacterial species used in this study, *Pseudomonas fluorescens* were measured as described by Zhao et al. (2007b).

Microbial assays

The assay is described in Akesso et al (2009). In brief, five replicate samples of each coating were immersed in a glass tank containing 500 ml of a suspension of P. fluorescens (10⁶ cells ml⁻¹), incubated on a shaker (20 rpm) at 28°C for 1 h. Each sample was dipped twice vertically in sterile distilled water with a custom-made automated dipper apparatus under a constant speed of 0.03 m s⁻¹ in order to remove loosely attached bacteria. To assess the adhesion strength of the attached bacteria, each sample was dipped a further 20 times vertically in a glass vessel (A) containing 130 ml sterile distilled water at 28°C at a constant shear stress of 0.014 N m⁻² and at a constant speed of 0.03 m s⁻¹. Each test sample was transferred to a second glass vessel (B) with 25 ml sterile distilled water at 28°C and sonicated in an ultrasonic bath to remove all the remaining attached bacteria. The total number of bacteria attached to the sample is the sum of the bacteria in vessel (A) and the bacteria in vessel (B). The percentage removal of bacteria from the sample is calculated from the number of bacteria in vessel (A) ie number removed by shear compared to the sum of the bacteria in vessel (A) and the bacteria in vessel (B) ie total attached. The number of bacteria in vessels (A) and (B) was determined by a standard plating method for

viable cell counts (Zhao et al. 2007b). For vessel (A), 100 µl of bacterial suspension from 130 ml vessel (A) as well as 10^{-1} and 10^{-2} dilutions were plated out onto tryptone-soya agar plates, respectively. The agar plates were incubated for 24 h at 28°C for viable cell counts. The number of bacteria in 100 µl of bacterial suspension was obtained using the appropriate concentration from original, 10^{-1} dilution or 10^{-2} dilution. Then the total number of bacteria in 130 ml in vessel (A) was calculated. The number of bacteria in 25 ml from vessel B was determined using the same method. The total number of bacteria, as colony-forming units (CFU) attached to the coating and the percentage removal from the coating was the mean of maximum 15 measurements, 3 from each of 5 replicate samples. Slides coated with a polydimethyl siloxane elastomer, Silastic® T2 (Dow Corming) supplied by TNO, The Netherlands, were included in the assay as standards.

RESULTS

Table 1 shows surface energy components of the DLC coatings and *Pseudomonas fluorescens* at 28 °C.

Table	1	surface	energy	components	of the	DLC	coatings				
and Pseudomonas fluorescens at 28 °C.											

Coatings/bacteria		Surface eneergy components [mN/m]				
Name	Chemistry	γ^{LW}	γ^+	γ^{-}	γ^{TOT}	
DLC1	1%Si-DLC	46.78	5.21	1.52	52.41	
DLC2	2%Si-DLC	47.43	0.96	8.05	52.99	
DLC3	3.8%Si-DLC	47.58	0.57	16.11	53.64	
DLC4	0.5%Si2.2N%-DLC	44.77	2.10	6.68	52.27	
DLC5	3.7%Si2.1N%-DLC	44.18	1.90	7.21	51.59	
DLC6	9.0%Si2.3N%-DLC	42.47	1.02	6.90	47.78	
DLC7	20%Si2.0N%-DLC	39.12	0.12	7.20	41.00	
	P. fluorescens	17.97	5.97	69.78	58.79	

Initial attachment of *Pseudomonas fluorescens* on the Si-and Si-N-doped DLC coatings (DLC1 - DLC7) is shown in Figure 1. The incorporation of 2%N into the Si-doped DLC coatings (DLC4, DLC5, DLC6, DLC7) significantly reduced bacterial attachment (p=0.05), compared with pure Si-DLC coatings (DLC1, DLC2, DLC3) and the PDMS standard, Silastic[®] T2. The incorporation of 2%N into the Si-doped DLC coatings also increased bacterial removal. Figure 2 indicates that for the first 3 Si-doped DLC coatings (DLC1, DLC2, DLC3), percent bacterial removal increased with increasing Si content in the DLC coatings ie adhesion strength decreased with increasing Si content in the DLC coatings. DLC1 (1%Si-DLC) was significantly different (p=0.05) to DLC2 (2%Si-DLC) and DLC3 (3.8%Si-DLC). Figure 6 also indicates that for the four Si-N-doped DLC

coatings (DLC4, DLC5, DLC6, DLC7), percent bacterial removal increased significantly with increasing Si content in the DLC coatings.



Figure 1: Comparison of formation of *pseudomonas* fluorescens cells on DLC coatings and on T2 silastic. N = 15, error bars are $2 \times$ Standard Error.



Figure 2: Comparison of removal of *pseudomonas* fluorescens cells on DLC coatings and on T2 silastic. N = 15, error bars are $2 \times$ Standard Error.

Figure 3 (a) Electron acceptor γ_s^+ vs bacterial removal for Si-doped DLC coatings; (b)electron acceptor γ_s^+ vs bacterial removal for Si-N-doped DLC coatings; (c) electron donor γ_s^- vs bacterial removal for Si-doped DLC coatings; (d) electron donor γ_s^- vs bacterial removal for Si-N-doped DLC coatings. N = 15, error bars are 2× Standard Error.



Figure 3 shows that percent bacterial removal strongly correlated with the surface energy components electron acceptor γ_s^+ and electron donor γ_s^- of the DLC coatings. *Pseudomonas fluorescens* had high value of γ_B^- component (69.78 mN/m) and low value of γ_B^+ component (5.97 mN/m), and would be negatively charged with the zeta potential of -16.1 mV (Azeredo et al. 2003). Chibowski et al. (1994) investigated the changes in zeta potential and surface energy components of calcium carbonate due to exposure to radiofrequency electric field. They observed that zeta potential decreased with an increase in the electron donor component γ_s of the surface energy. The observed changes in zeta potential and surface free energy components were believed to result from changes in the surface charge of calcium carbonate (Chibowski et al. 1994). These observations may explain why bacterial removal decreased with increasing electron acceptor γ_s^+ values of the DLC coatings (Fig 3a, 3b) and increased with increasing electron donor γ_s^- values of DLC coatings (Fig. 3c, 3d).

DISCUSSION

Bacterial adhesion strength can be explained in terms of work of adhesion, which is Sharma and Rao (2002) defined as:

$$\Delta F_{Adh} = \gamma_{SB} - \gamma_{SL} - \gamma_{BL} \tag{1}$$

where ΔF_{Adh} is the interfacial free energy of adhesion. γ_{SB} is the solid-bacterium interfacial free energy, γ_{SL} is the solid-liquid interfacial free energy, and γ_{BL} is the bacterium-liquid interfacial free energy. The ΔF_{Adh} calculation needs values for γ_{SB} , γ_{SL} and γ_{BL} which can be calculated from measured contact angle data and the van Oss Acid-Base approach. The interfacial tension between substances i and j is generally expressed as (van Oss 1994):

$$\gamma_{ij} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}}\right)^2 + 2\left(\sqrt{\gamma_i^+} - \sqrt{\gamma_j^+}\right)\left(\sqrt{\gamma_i^-} - \sqrt{\gamma_j^-}\right).$$
(2)

Therefore, the work of adhesion can be further expressed by:

$$\Delta F_{Adh} = 2(\sqrt{\gamma_s^{LW} \gamma_L^{UW}} + \sqrt{\gamma_s^{+} \gamma_L^{-}} + \sqrt{\gamma_s^{-} \gamma_L^{+}} + \sqrt{\gamma_B^{LW} \gamma_L^{LW}} + \sqrt{\gamma_B^{+} \gamma_L^{-}} + \sqrt{\gamma_B^{-} \gamma_L^{+}} - \sqrt{\gamma_s^{LW} \gamma_B^{LW}} - \sqrt{\gamma_s^{+} \gamma_B^{-}} - \sqrt{\gamma_s^{-} \gamma_B^{+}} - \gamma_L)$$
(3)

Like all systems in nature, this system will also proceed in the direction of lowering the total energy, which means that adhesion is favored if ΔF_{Adh} is negative as a result of adhesion. If ΔF_{Adh} is positive, adhesion is thermodynamically unfavorable. Therefore, bacterial adhesion strength should decrease when work of adhesion ΔF_{Adh} increases.

The work of adhesion ΔF_{Adh} for *Pseudomonas* fluorescens cells adhered to the DLC coatings was calculated from the data for the surface energy components in Tables 1. Figure 4 shows there is a strong correlation between the removal of *Pseudomonas fluorescens* cells and work of adhesion for both the Si-doped DLC coatings and for Si-N-doped DLC coatings. The results show that bacterial adhesion decreased with increasing work of adhesion, which is consistent with the thermodynamic theory.

The experimental results showed that bacterial removal decreased with increasing electron acceptor γ_s^+ values for the DLC coatings, but increased with increasing electron donor γ_s^- values. Zhao et al (2004) investigated the effect of increasing surface temperature on surface energy components of DLC coatings and stainless steel. They found that γ_s^+ increased with increasing surface temperature, but the γ_s^- component decreased with increasing surface temperature. This indicates that bacterial adhesion strength probably increases with increasing surface temperature.

In this investigation two types of the DLC coatings The Si-doped DLC coatings (DLC1 were produced. DLC3) were produced by an unbalanced magnetron sputter ion-plating combined with PECVD. The Si in the DLC coatings was achieved by sputtering a solid Si target, while the Si-N-doped DLC coatings (DLC4 - DLC7) were produced by radio frequency PECVD and the Si in the DLC coatings was from the Si(CH₃)₄ gas. The experimental results showed that the Si-N-doped DLC coatings performed more efficiently than Si-doped DLC coatings both in reducing bacterial attachment and in removal by shear. Clearly the incorporation of 2%N into the Si-doped DLC coatings considerably improved the performance of the coatings. As well as the addition of 2%N, the PECVD coating method and the Si source from Si(CH₃)₄ gas may also lead to the improvement in performance of Si-N-doped DLC coatings. More detailed research will be carried out to investigate the effect of surface chemistry and coating methods on the performance of modified DLC coatings.

Diamond-like carbon (DLC) coatings have favourable properties, such as excellent thermal conductivity similar to metals, low friction, extremely smooth surface, hardness, wear resistance and corrosion resistance, which are very suitable for heat exchanger applications. It has already demonstrated that DLC coatings reduce the formation of hard mineral scale on heat transfer surfaces and have potential for heat exchanger application (Förster and Bohnet 1999; Zhao and Wang 2005). This investigation further demonstrats that the modified DLC coatings have the potential to reduce biofouling in heat exchangers.



Figure 4: Removal of *Pseudomonas fluorescens* cells vs work of adhesion ΔF_{Adh} for Si-doped DLC coatings (a) and for Si-N-doped DLC coatings (b)

CONCLUSIONS

- 1. Bacterial removal increased with increasing Si content in the DLC coatings
- The incorporation of 2%N into the Si-doped DLC coatings significantly reduced bacterial attachment, compared with pure Si-DLC coatings
- 3. Bacterial adhesion decreased with increasing work of adhesion, which is consistent with the thermodynamic theory.

NOMENCLATURE

 γ^+ electron acceptor, mN/m

 γ^- electron donor, mN/m

 γ^{LW} Lifshitz-van der Waals apolar component, mN/m

 γ^{TOT} Total surface free energy, mN/m

 ΔF_{Adh} interfacial free energy of adhesion, mN/m

Subscript

- B bacteria
- L Liquid
- S Surface or coating

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