

DEVELOPMENT AND EVALUATION OF Ni–Cu–P–PTFE COMPOSITE COATINGS TO MINIMIZE MICROBIAL ADHESION

Q. Zhao^{1,*}, Y. Liu¹, C. Wang¹, S. Wang¹ and H. Müller-Steinhagen²

¹ Department of Mechanical Engineering, University of Dundee, Dundee, DD1 4HN, UK. E-mail: Q.Zhao@dundee.ac.uk

² Institute for Thermodynamics and Thermal Engineering, University of Stuttgart, D-7000, Stuttgart, Germany

² Institute for Technical Thermodynamics, German Aerospace Centre. Email: Hans.Mueller-Steinhagen@dlr.de

ABSTRACT

In this paper a cost-effective Ni–Cu–P–PTFE composite coating with corrosion-resistant properties was developed by an auto-catalytic plating technique to minimize bacterial adhesion. The experimental results showed that the surface free energy of the Ni–Cu–P–PTFE coatings, which was altered by changing the PTFE content in the coatings, had a significant influence on bacterial adhesion. The Ni–Cu–P–PTFE coatings with surface free energy in the range 21–25.3 mJ/m² reduced the adhesion of *E. coli Rosetta* by over 96–98%, compared with stainless steel or titanium surfaces. The interaction energies between *E. coli* and the coatings were calculated with the extended DLVO theory. It was found that there was a strong correlation between the bacterial adhesion and the interaction energies or surface free energies of the coatings.

1. INTRODUCTION

Biofouling on the surfaces of pipelines and heat exchangers in cooling water systems is a widespread problem. It not only reduces heat transfer performance significantly, but also causes considerable pressure drop, calling for higher pumping requirements. Since microbial adhesion on the surfaces is a prerequisite for biofouling formation, prevention of microbial adhesion on the equipment surfaces will have a major impact in preventing biofouling. An effective and desired approach to reduce cooling water biofouling is to alter the surface properties of the equipment and to make it less attractive for the fouling components, so that they can be removed easily from the surfaces by flowing water. The surface free energy of a solid surface gives a direct measure of intermolecular or interfacial attractive forces. Over the past two decades, marine bacterial adhesion to surfaces with different surface free energies has been investigated with the frequent conclusion that bacterial adhesion is less to low energy surfaces and easier to clean because of weaker binding at the interface (Dexter et al, 1975; Hamza et. al. 1997).

Many attempts have been made to reduce fouling by coating surfaces with PTFE due to its low surface energy with non-stick properties. However, the poor thermal conductivity, poor abrasion resistance and poor adhesion to

metal substrates of the PTFE coatings currently inhibit their commercial use (Müller-Steinhagen and Zhao, 1997). The first electroless Ni–P–PTFE composite coatings were introduced about 24 years ago (Tulsi, 1983). The incorporation of PTFE nanoparticles into the Ni–P matrix can take advantage of the different properties of Ni–P alloy and PTFE. It has been demonstrated that the Ni–P–PTFE coated heat transfer surfaces have anti-fouling properties (Zhao et al, 2002). Because the electroless Ni–P–PTFE coatings are metal-based, their thermal conductivity, anti-abrasive property, mechanical strength and adhesive strength to the substrate are superior to standard PTFE coatings. However, the corrosion resistance of the Ni–P–PTFE coatings needs to be improved, since parts of the Ni–P–PTFE coatings were found to peel-off during long-term fouling tests with seawater due to corrosion. It was reported that the addition of copper into the electroless Ni–P matrix improved the corrosion resistance of the Ni–Cu–P coatings (Armyanov et. al, 1999). In the present investigation, the corrosion rates of the Ni–Cu–P–PTFE composite coatings in NaCl solutions and the effects of surface free energy of Ni–Cu–P–PTFE coatings on the adhesion of *E. coli Rosetta* were investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Ni–Cu–P–PTFE composite coatings

To improve coating adhesion and corrosion resistance, graded Ni–P/Ni–Cu–P/Ni–Cu–P–PTFE layers were coated on the stainless steel 304 surfaces of 10mm × 15mm × 1.0 mm. The interlayer thickness of Ni–P/Ni–Cu–P was 2 μm. The Ni–Cu–P–PTFE composite coating was prepared by gradually increasing the PTFE content from the Ni–Cu–P interlayer to the top surface. Since there is no obvious interface between the coatings, the coating adhesion is improved significantly. The stainless steel samples were first cleaned with alkaline solution at 60–80°C for 10–20 minutes and then rinsed with water. They were dipped into a dilute HCl solution (1 M) for 30 s and then rinsed with cold water and deionized water, respectively. The composition of electroless Ni–Cu–P–PTFE solutions used in this investigation included 50 g/l NiSO₄·6H₂O; 1.0 g/l CuSO₄·5H₂O; 60 g/l Na₃C₆H₅O₇·2H₂O; 25 g/l

* Corresponding author. Tel: +44-1382-345651; fax: +44-1382-345508; E-mail address: Q.Zhao@dundee.ac.uk

NaH₂PO₄·H₂O; 40 g/l NH₄CH₃COO; 4–18 ml/l PTFE (60 wt.%) and 0 – 0.6 g/l cationic surfactant. A 60% PTFE emulsion from Aldrich with a particle size in the range 0.05–0.5 μm and a cationic surfactant were diluted with deionized water and stirred with a magnetic stirrer for 1 hour. Then the solution was filtered with a filter of pore size 0.2 μm before use. PTFE particles in the baths were dispersed uniformly by the surfactant without using any mechanical agitation or ultrasonic homogeniser. The coating thickness was measured using a digital micrometer and the coating compositions were analysed with an energy dispersive X-ray microanalysis (EDX) model JEOL T-300 at beam energy of 20 keV.

2.2 Corrosion rate measurement

The coatings were submerged in stagnant NaCl solution with various concentrations at room temperature for 2 months. The corrosion rates of the coatings in the NaCl solutions were measured by a weight loss technique using a precise electric balance (resolution 10⁻⁵ g) and were compared with those of electroless Ni–P, Ni–P–PTFE, AISI 1020 low-carbon steel, stainless steel 304 and copper plates.

2.3 Contact angle measurements

Prior to contact angle measurement, samples were ultrasonically cleaned in acetone, ethanol and deionized water in sequence. Contact angles were obtained using the sessile drop method with a Dataphysics OCA-20 contact angle analyser. This instrument consists of a CCD video camera with a resolution of 768×576 pixel and up to 50 images per second, multiple dosing/micro-syringe units and a temperature controlled environmental chamber. The drop image was processed by an image analysis system, which calculated both the left- and right contact angles from the shape of the drop with an accuracy of ± 0.1°. Three test liquids were used as a probe for surface free energy calculations: distilled water, diiodomethane (Sigma) and ethylene glycol (Sigma). The contact angle of bacterial cells was measured on the lawns of bacteria deposited on membrane filters with pore diameter of 0.45 μm. Prior to contact angle measurement, the bacterial lawns were dried in air to a certain state, indicated by stable water contact angles. Usually this state of drying of a microbial lawn lasts 30–60 minutes and indicates that only bound water is present on the surface.

2.4 Surface free energy

The theory of contact angle of pure liquids on a solid was developed 200 years ago in terms of the Young equation (Young, 1805):

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (1)$$

where γ_L is the experimentally determined surface tension of the liquid, θ is the contact angle, γ_S is the surface free energy of the solid and γ_{SL} is the solid/liquid interfacial energy. van Oss et al. (1988) developed an acid-base approach for the calculation of surface free energy. The surface free energy is seen as the sum of a Lifshitz-van der Waals apolar component γ_i^{LW} and a Lewis acid-base polar component γ_i^{AB} :

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (2)$$

The acid-base polar component γ_i^{AB} can be further subdivided by using specific terms for an electron donor (γ_i^-) and an electron acceptor (γ_i^+) subcomponent:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad (3)$$

The solid/liquid interfacial energy is then given by:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + \sqrt{\gamma_S^+ \cdot \gamma_L^-} + \sqrt{\gamma_S^- \cdot \gamma_L^+}) \quad (4)$$

Combining this with the Young equation (1), a relation between the measured contact angle and the solid and liquid surface free energy terms can be obtained:

$$\gamma_L \cdot (1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + \sqrt{\gamma_S^+ \cdot \gamma_L^-} + \sqrt{\gamma_S^- \cdot \gamma_L^+}) \quad (5)$$

In order to determine the surface free energy components (γ_S^{LW}) and parameters γ_S^+ and γ_S^- of a solid, the contact angles of at least three liquids with known surface tension components (γ_L^{LW} , γ_L^+ , γ_L^-), two of which must be polar, have to be determined.

2.5 Bacterial adhesion

In this investigation, *Escherichia coli* (*E. coli*) *Rosetta* from the Wellcome Trust Bio-Center of the University of Dundee were used for bacterial adhesion tests. A standard membrane filtration method was used to quantify the number of the bacterial colonies or colonies forming units (CFU) attaching to the treated and untreated surfaces (AWWA, 1998). After the frozen *E. coli* *Rosetta* was defrosted, it was cultured in petri dishes with Luria-Bertani (LB) agar at 36.4°C over night, and then colonized in 5ml LB broth at 37°C for 8 hours. Finally, 5ml *E. coli* *Rosetta* was diluted in 50ml sterile deionised water. The samples were exposed to the cell suspensions of *E. coli* *Rosetta* (about 1.9×10⁹ cells/ml) in a beaker on a shaker 20–30 rpm for 5 hours at 37°C. These samples were taken out and

were put into 100 ml sterile deionised water. Then they were stirred in order to remove the adhered bacteria into the water thoroughly. Then the water passed through membrane filters with a pore size 0.45µm and *E. coli* remained on the filter surfaces. When the filters were replaced on growth medium-membrane lauryl sulphate broth (MLSb) in petri dishes, the bacteria formed a small visible colony after 24 h incubation at 44°C. The incubation at 44°C is to promote growth of *E. coli* and inhibit growth of other non-thermotolerant bacteria. The numbers of *E. coli* on the filters were counted. If the water contained a large amount of bacteria, it needed to be diluted several times with a Ringer solution in order to facilitate counting. Finally, the number of *E. coli* colonies (CFU/cm²) on the surfaces was calculated.

3. RESULTS

3.1 Ni–Cu–P–PTFE composite coatings

The thickness of the graded Ni–Cu–P–PTFE composite coatings was about 22 µm, including the 2 µm Ni–P/Ni–Cu–P interlayer. The compositions of the Ni–Cu–P–PTFE composite coatings were analysed with an energy dispersive X-ray microanalysis. Figure 1 shows typical elemental compositions of the electroless Ni–Cu–P–PTFE composite coatings. The PTFE content was calculated based on the fluorine content in the coating.

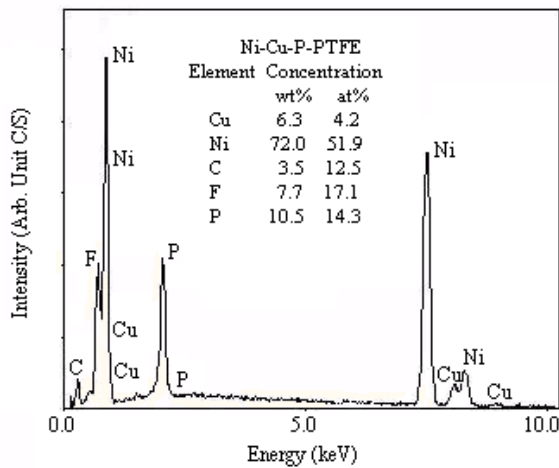


Fig. 1 EDX energy and element compositions for Ni–Cu–P–PTFE coating

3.2 Corrosion rate measurement

Fig. 2 shows the comparison of corrosion rates of AISI 1020 low-carbon steel, copper, stainless steel 304, Ni–P, graded Ni–P/Ni–P–PTFE and graded Ni–P/Ni–Cu–P/ Ni–Cu–P–PTFE in NaCl solutions with concentrations of 3.5

wt%, 7 wt%, 10 wt%, 15 wt% and 20 wt%, respectively. The corrosion rate of the Ni–Cu–P–PTFE coating was much lower than those of AISI 1020 low-carbon steel, copper, stainless steel 304, Ni–P coating and Ni–P–PTFE coating. The incorporation of copper into Ni–P–PTFE matrix improved the corrosion-resisting properties of the coatings.

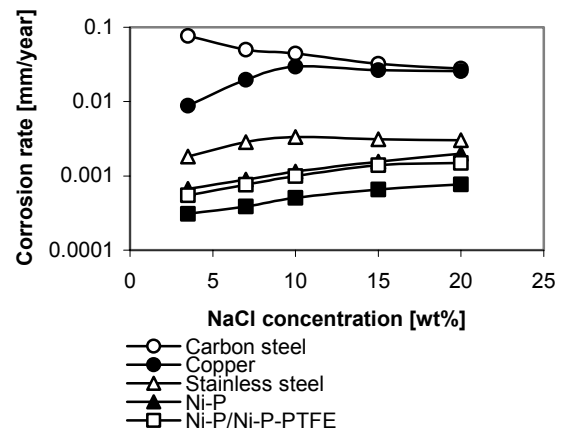


Fig.2 Comparison of graded Ni–Cu–P–PTFE with carbon steel, copper, stainless steel 304, Ni–P and Ni–P–PTFE with respect to inhibiting NaCl corrosion at 20 °C

3.3 Surface free energies

Contact angles of test liquids, distilled water (θ^W), diiodomethane (θ^D) and ethylene glycol (θ^{EG}) on Ni–Cu–P–PTFE coatings with various PTFE contents, Ni–P coating, stainless steel 304 sheets, stainless steel 316L sheets, titanium sheets and *E. coli Rosetta* were measured. According to the contact angle values, the surface energies of the samples and their dispersive and polar components were calculated using the van Oss acid-base approach. The results are given in Table 1. Table 1 shows that the surface energy of Ni–Cu–P–PTFE coatings decreases significantly with increasing PTFE content in the coatings.

3.4 Bacterial adhesion

Fig. 3 shows the comparison of the numbers of cell colonies attached to the Ni–Cu–P–PTFE coated surface (PTFE 10.1 wt%; $\gamma_S = 21.19$ mJ/m²), the Ni–Cu–P–PTFE coated surface (PTFE 8.2 wt%; $\gamma_S = 25.3$ mJ/m²), the Ni–P coated surface ($\gamma_S = 34.97$ mJ/m²), the stainless steel 304 sheet ($\gamma_S = 39.62$ mJ/m²), the stainless steel 316L sheet

($\gamma_s = 40.71 \text{ mJ/m}^2$) and the titanium sheet ($\gamma_s = 43.89 \text{ mJ/m}^2$) over a contact time of 5 hours. The PTFE content in the coatings was only increased from 8.2 to 10.1 %, but the surface energy reduced to 21.11 mJ/m^2 from 25.3 mJ/m^2 . The number of cell colonies attached to the surfaces decreased with decreasing surface energy and reached a minimum when the surface energy of the coatings was in the range of 21 - 25 mJ/m^2 . The Ni-Cu-P-PTFE coated surfaces performed best in inhibiting *E. coli* attachment, compared with stainless steel 304, stainless steel 316L, titanium or Ni-P coatings.

Table 1 The surface energy components of samples

Surfaces/bacteria	Surface energy components				
	[mJ/m^2]				
	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{TOT}
Ni-Cu-P-PTFE (PTFE: 10.1 wt%)	21.19	0.00	0.00	0.00	21.19
Ni-Cu-P-PTFE (PTFE: 8.2 wt%)	25.30	0.00	0.00	0.00	25.30
Ni-P	33.55	0.07	7.21	1.42	34.97
Stainless steel 304	39.62	0.00	18.43	0.00	39.62
Stainless steel 316L	39.00	0.02	36.39	1.71	40.71
Titanium	41.32	0.04	41.14	2.57	43.89
<i>E. coli</i> Rosetta	35.60	0.14	67.68	6.16	41.76

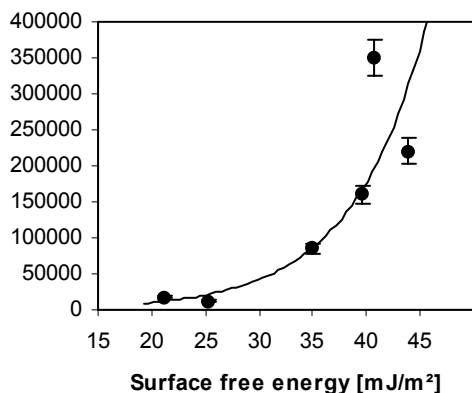


Fig. 3 Effect of surface free energy on *E. coli* Rosetta attachment over a contact time of 5 hours at 37°C

4. DISCUSSION

The first theory used to explain bacterial adhesion onto solid surfaces was the DLVO theory, named after four scientists, Derjaguin, Landau, Verwey and Overbeek

(Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). van Oss (1994) proposed an extension of the DLVO theory, generally known as extended DLVO theory. The principle interaction forces determining hetero-coagulation by the extended DLVO theory include a Lifshitz-van der Waals (LW) attractive interaction component, an electrostatic double-layer repulsive component (EL), a Lewis acid-base component (AB), and a Brownian motion component (Br). The total interaction energy ΔE^{TOT} between a particle and a solid surface can be written as the sum of these corresponding interaction terms:

$$\Delta E^{TOT} = \Delta E^{LW} + \Delta E^{EL} + \Delta E^{AB} + \Delta E^{Br} \quad (6)$$

Recently, Azeredo, Visser and Oliveira (1999) and Oliveira (1997) suggested that the balance between all possible interactions determines whether or not a particle (or bacterium) attaches on the surface: adhesion will take place when ΔE^{TOT} is negative (i.e. total interaction force is attractive).

4.1 Lifshitz-van der Waals interaction

For the interaction energy between a sphere of radius R (particle 1) and a flat surface 2 in medium 3 (e.g. water), the Lifshitz-van der Waals interaction energy can be calculated using the following equation:

$$\Delta E^{LW} = -\frac{24\pi H_0^2 (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}}) \cdot R}{6H} \quad (7)$$

where H_0 is the minimum equilibrium distance between the two interacting bodies, which has been found for a large range of materials to be equal to 0.157nm. γ_i^{LW} values of solid surfaces and bacteria used in this study were measured and are given in Table 1.

4.2 Electrostatic Double-Layer interaction

The electrostatic double layer interaction term ΔE^{EL} between sphere 1 (bacteria) and flat surface 2 (coated surface) is given by Eq. (12) when the interaction takes place at constant surface potential ϕ (Azeredo, Visser and Oliveira, 1999; Oliveira, 1997).

$$\Delta E^{EL} = \varepsilon\pi R \left\{ \begin{aligned} &(\phi_1 + \phi_2)^2 \ln[1 + \exp(-\kappa H)] \\ &+ (\phi_1 - \phi_2)^2 \ln[1 - \exp(-\kappa H)] \end{aligned} \right\} \quad (8)$$

where ϕ_1 and ϕ_2 are the electrical surface potential of the spherical particle (e.g. bacterium) and the flat surface (e.g. coated surface); R is the sphere radius; ε is the electrical permittivity of the medium or solution and κ is the

reciprocal double-layer thickness, or *Debye-Hückel* parameter ($1/\kappa = 1.1\text{nm}$). Since the surface potential ϕ can not be determined experimentally, it is usually replaced by the zeta potential.

4.3 Lewis acid-base interaction

van Oss (1994) extended the DLVO theory by including the Lewis acid/base interaction. The contribution of ΔE^{AB} to the overall interaction energy ΔE^{TOT} between sphere 1 (e.g. bacterium) and flat surface 2 (e.g. coated surface) in liquid medium 3 (e.g. water) is given by:

$$\Delta E^{AB} = 2\pi R\lambda\Delta E_{132}^{AB} \exp\left(\frac{H_0 - H}{\lambda}\right) \quad (9)$$

where λ is the decay-length pertaining to water molecules, approximately equal to 0.2 nm for pure water (Oliveira 1997), H_0 is the equilibrium distance and H is the distance.

ΔE_{132}^{AB} is a function of the electro donor (γ^-) and electro acceptor (γ^+) parameters of the polar component (γ^{AB}) of the surface tension of interacting bodies. It can be expressed as:

$$\Delta E_{132}^{AB} = 2 \left[\sqrt{\gamma_3^+} \cdot (\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-}) + \sqrt{\gamma_3^-} \cdot (\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+}) - \sqrt{\gamma_1^+ \cdot \gamma_2^-} - \sqrt{\gamma_1^- \cdot \gamma_2^+} \right] \quad (10)$$

For water $\gamma_3^+ = \gamma_3^- = 25.5 \text{ mJ/m}^2$.

4.4 Brownian Motion

Particles (e.g. bacteria) adhering to a surface have two instead of three degrees of freedom, as one perpendicular to the surface has been blocked by bonding. Since Brownian motion comprise $\frac{1}{2} kT$ per degree of freedom, the corresponding free energy term ΔE^{Br} of a particle adhering to a surface equals $1 kT = 0.414 \times 10^{-20} \text{ J}$ at 300 K (Oliveira, 1997).

$$\Delta E^{Br} = 0.414 \times 10^{-20} \text{ J} \quad (11)$$

The total interaction energy ΔE^{TOT} and their components (ΔE^{LW} , ΔE^{EL} , ΔE^{AB} , ΔE^{Br}) between the *E. coli* and various solid surfaces in water were calculated using the above equations. The radius and zeta potential of *E. coli* were assumed to be $0.65\mu\text{m}$ (Li and Logan, 2004) and -5.4 mV (Chen and Strevett, 2003), respectively. The distance of H was taken as 4 nm. Zeta potential of the materials used in this investigation was around -25 mV . Fig. 4 shows the effect of the total interaction energy ΔE^{TOT} on the cell adhesion. The numbers of cell colonies attached to the surfaces decrease with increasing total interaction energy

ΔE^{TOT} . The higher the total interaction energy ΔE^{TOT} , the more repulsive the coatings are to the bacteria.

Fig.5 shows that the total interaction energy ΔE^{TOT} increases linearly with decreasing surface free energy γ_s . According to the extended DLVO theory, the bacterial adhesion decreases with increasing total interaction energy ΔE^{TOT} . Fig. 5 explains why the numbers of cell colonies attaching to the surfaces decreases with decreasing free energy of the surfaces under the experimental conditions.

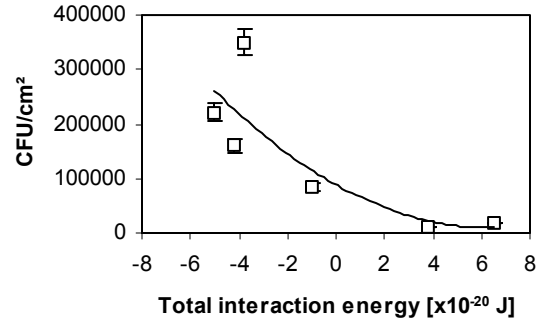


Fig. 4 Effect of total interaction energy ΔE^{TOT} on *E. coli Rosetta* attachment

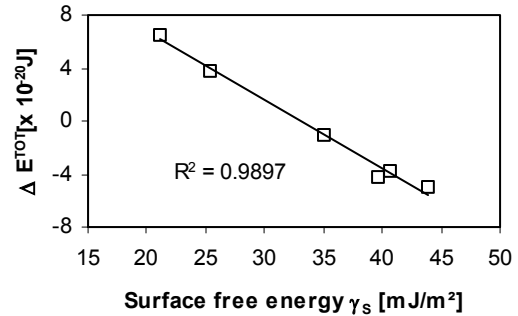


Fig. 5 Total interaction energy ΔE^{TOT} vs surface free energy γ_s .

5. CONCLUSIONS

- 1) The surface free energy of Ni-Cu-P-PTFE coatings decreased with increasing PTFE content in the coatings.
- 2) The number of cell colonies attaching to the surfaces with various surface energies decreased with decreasing surface free energies or with increasing total interaction energy ΔE^{TOT} . There exists a good correlation between

the experimental measurements and the calculation from the extended DLVO theory.

- 3) The electroless Ni–Cu–P–PTFE composite coatings showed excellent anti-microbial properties. When the surface free energy of the Ni–Cu–P–PTFE coated surfaces was in the range of 21–25 mJ/m², bacterial adhesion reached a minimum.

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NOMENCLATURE

A	Hamaker constant
ΔE	Interaction energy, J
H	Separation distance, m
R	Radius, m
θ	Contact angle, °
γ	Surface tension or surface free energy; mN/m
ϕ	Electrical surface potential, V

Subscript

1	Bacteria
2	Solid surfaces, coatings
3	Media, water
L	Liquid
S	Surface

REFERENCES

- Armyanov, S., Georgieva, J., Tachev, D., Valova, E., Nyagolova, N., Mehta, S., Leibman, D., Ruffini, A., (1999). Electroless deposition of Ni–Cu–P alloys in acidic solutions. *Electrochemical and Solid State Letters* 2, 323–325.
- AWWA, Standard Methods for the Examination of Water and Wastewater (1998), 20th Edition.
- Azeredo, J., Visser, J., Oliveira, R., (1999). Exopolymers in bacterial adhesion: interpretation in terms of DLVO and XDLVO theories. *Colloid. Surf. B-Biointerfaces* 14, 141–148.
- Chen, G., Strevett, K.A., (2003). Microbial surface thermodynamics and interactions in aqueous media. *J. Colloid Interface Sci.* 261,283–290.
- Derjaguin, B.V., Landau, L., (1941), *Acta Physicochim.* 14, 633–662.
- Dexter, S.C., Sullivan, J.D., Williams, J., Watson, S.W., (1975). Influence of substrate wettability on the attachment of marine bacteria to various surfaces. *Applied Microbiology* 30, 298–308.
- Hamza, A., Pham, V.A., Matsuura, T., Santerre, J.P., (1997). Development of membranes with low surface energy to reduce the fouling in ultrafiltration applications. *Journal of Membrane Science* 131, 217–227.
- Li BK, Logan B.E., (2004). Bacterial adhesion to glass and metal-oxide surfaces. *Colloid. Surf. B-Biointerfaces* 36,81–90.
- Müller-Steinhagen, H., Zhao, Q., (1997). Investigation of low fouling surface alloys made by ion implantation technology. *Chemical Engineering Science* 52, 3321–3332.
- Oliveira, R., (1997). Understanding adhesion: a means for preventing fouling. *Experimental Thermal and Fluid Science* 14, 316–322.
- Tulsi, S.S., (1983). Composite PTFE-nickel coatings for low friction applications. *Finishing* 7, 14–18.
- Zhao, Q., Liu, Y., Muller-Steinhagen, H., Liu, G., (2002). Graded Ni-P-PTFE coatings and their potential applications, *Surf. Coat. Tech.* 155,279–284.
- van Oss, C.J. (1994). *Interfacial Forces in Aqueous Media*. Marcel Dekker, New York.
- van Oss, C.J., Good, R.J., Chaundhury, M.K., (1988). Additive and nonadditive surface-tension components and the interpretation of contact angles. *Langmuir* 4, 884–891.
- Verwey, E.J.W., Overbeek, J.T.G. (1948), *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam.
- Young, T., (1805). An essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society, London* 95, 65–87.