Engineering nanoscale roughness on hydrophobic surface—preliminary assessment of fouling behaviour

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Received 12 January 2005; revised 9 March 2005; accepted 9 March 2005
Available online 20 June 2005

Abstract

A preliminary investigation of the fouling behaviour of smooth and roughened superhydrophobic coatings is reported. The effect of nanoscale interfacial roughness on the adhesion of single (SW8) and mixed cultures of micro-foulant for periods of up to 6 months was assessed using visual and wettability measurements. Detailed analysis indicated virtually no micro-organism attached to the superhydrophobic surfaces in the first weeks of immersion. As a result by comparison with smooth substrates, which exhibited fouling within a day, very rough (roughness ratio \(r_2 \geq 2.7\)) surfaces exhibited high resistance to fouling over a 6-month period. However, after periods exceeding 2 months under ocean conditions, both films showed limited anti-fouling properties. There appears to be a correlation between the nature of the nanoscale roughness in the creation of superhydrophobic coatings and their potential anti-fouling properties. The future architecture of such a correlation is investigated.

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Keywords: Anti-fouling; Superhydrophobic; Contact angle; Surface roughness

1. Introduction

The control of marine biofouling is of considerable interest both technically and economically [1–3]. Traditionally anti-fouling paints and coatings are designed with the biological nature of ‘pest’ in mind and typically are formulated to continuously release poisons, mostly based on heavy metals such as tin or copper [2,4]. Although successful in providing effective long-term anti-fouling performance, the anti-fouling biocides released from the paints are now recognised to cause adverse impacts in the marine environment and are increasingly posing risks to human health. As a result, biocides containing organotin have recently been reported [5], and copper-based anti-fouling paints are now under scrutiny [6].

These concerns have lead to a search for alternatives. One approach is to remove poisons altogether and focus on non-stick surfaces. Recent advances in paint and surface technology has produced a range of superhydrophobic coatings that have water contact angle of greater than 150\(^\circ\) [7,8]. The aim of this work is to investigate their potential to be applied as anti-foulants.

Anti-fouling coatings act through a combination of biological (poison) deterrents and chemical (non-stick) incompatibility. In the present work, the latter aspect is explored. The ‘chemical design’ of such interfaces can be modified through the adjustment of micro- and nanostructure. This allows naturally hydrophobic surfaces [contact angle (CA) < 90\(^\circ\)] to become superhydrophobic (CA > 150\(^\circ\)). Evaluation of this change to the fouling properties of these materials examined.

2. Experiment

Superhydrophobic material was made from fumed silica (primary particle size around 50 nm), alkyltrialkoxysilane and polysiloxane. A detailed description of the preparation method was described elsewhere [7,8]. Three superhydrophobic films having variations on chemistry and surface geometry were prepared. The chemical, surface structural
features, and water resistance of the film together with the standard polytetrafluoroethylene (PTFE) particle treated surface are summarised in Table 1. Thin film samples were prepared by dip coating glass microscope slides.

The roughness of these films was characterised using atomic force microscope (Dimension-3000 AFM). Tapping mode was selected during analysis at an analytical range of 5 μm. The resulting roughness ratio \( r \) is calculated by dividing surface area by projected surface area [9].

Macroscopic fouling behaviour assessed through short- and long-term fouling attachment tests described are below.

An **Immersion test** investigated the correlation between fouling and the change of wettability on surfaces after submerging in tap water for 1 day, 6 days, 21 days and 6 months. Surfaces were exposed to mixed cultures of naturally occurring micro-foulant in mains water. Contact angle was used as the quantitative indicator of changing surface hydrophobicity.

A **Static test** further examined surfaces remaining hydrophobic after 1 day immersion. These were exposed to a sole culture SW8 in artificial seawater for 10 min. The number of attached bacteria was determined using an epifluoroscene microscope. This provides a rapid assessment of the likelihood of long-term fouling properties.

In **Field-trial experiments** long-term through immersion in seawater was tested for 2 months [10]. Observation of fouling attachment was carried out after 1 and 2 months.

## 3. Results and discussion

### 3.1. Anti-fouling and the roughness of a hydrophobic surface

Non-wet area after immersion for a certain period of time has been estimated and the results summarised in Fig. 1. Contact angles were also measured before and after the immersion test and the results are shown in Fig. 2.

It was found that contact angles of surfaces with \( r < 2 \) decreased drastically with increasing immersion time. The decrease of contact angle is an indicator of loss of both hydrophobicity and roughness. Hydrophobic surfaces with \( r \approx 2.7 \) suggests micro- and nano-scale roughness (Fig. 4). This multi-level roughness has the direct contribution to the control of fouling as described in the following sections.

Previous studies [11] have shown that when superhydrophobic surfaces are immersed, air bubbles are entrapped into micro- and nano-sized pores at the solid surface. A mix of solid–liquid and solid–gas interfaces is created. The extent of solid–gas interface is proportional to the degree of hydrophobicity of the material. The higher the hydrophobicity, the larger the solid–gas interface will be.

The air bubble layer creates a barrier that may prevent adsorption of micro-organisms in the short-term. In the early stage of the immersion, air bubbles occupy most of the surface. With increasing immersion time, organisms displace the air. The net effect is the creation of a new solid–liquid interface to replace the original solid–gas interface.

The key is the design of surfaces that effectively ‘hold’ the air in place.

The amount of air bubbles attracted on hydrophobic surface depends on surface roughness. The rougher the surface, large percentage of solid–gas interface is created. However, the resistance of that layer to micro-organisms will depend on the design of the air adsorption sites.

Loss of superhydrophobicity occurs in a variety of ways. One way is that air may be dissolved in water for a long-term period submersion. More importantly, it occurs when the chemistry or structure of surface is changed due to

| Chemical composition | Roughness ratio | Contact angle (degrees) |
|----------------------|-----------------|------------------------|
| Polysiloxane         | 1.1             | 75                     |
| PTFE particles       | 1.3             | 150                    |
| Polysiloxane and fine particles | 2.7 | 169                    |

**Table 1** Surfaces for fouling attachment tests

**Fig. 2.** Change on contact angles before and after the immersion test.

**Fig. 1.** Wetting behaviour after immersion.
3.2. Short-term anti-fouling properties of superhydrophobic surfaces

The static test provides a direct method to determine the amount of bacteria attached to the surface under standard conditions. The photos shown in Fig. 3 were taken under epifluoroscene microscope. Quantification of the number of the micro-organism attached on surface leads to the comparison between a hydrophobic and a superhydrophobic surface.

It has been found that, in a 10 min period there is only one visible bacterium in view on rough polysiloxane surfaces while on smooth polysiloxane surface considerably more have been attracted.

Rough polysiloxane surfaces therefore have a better anti-fouling performance due to the combination of its unique geometrical feature on surface and chemical origin of low surface energy material. It was shown under AFM (Fig. 4) that such a surface presents extreme roughness $r \sim 2.7$ which is much larger than that of a smooth surface. The actual surface in contact with water, and the area for delivery of the micro-organism is largely reduced due to the attraction of air bubbles. Such effects lead to a persistence in anti-fouling performance over short periods of time. This result is consistent with that obtained from the immersion test.

The conditioning film which precedes full scale colonisation usually contains macromolecules and proteins, which change the overall surface chemistry.

3.3. Long-term anti-fouling properties of superhydrophobic surfaces

After 1 month of immersion, coatings with nanoscale rough polysiloxane surfaces accumulate only a small coverage of green algae (<5% surface cover) and few barnacles (<2% cover) (Fig. 5). Closer inspection shows signs of fish grazing, particularly near the edges of the test surface.

The observation that fish appeared attracted to the test surfaces is of interest. It is assumed that the attraction is initiated by the attached nutrients, and the subsequent lack of adhesion of the micro-organism layer to the coating makes it easier to remove the ‘food’. It suggests that the contamination has weak interaction with the coating surface. This secondary mechanism may also explain the reduced barnacle numbers on the test surfaces with natural cleaning through fish grazing rather than first stage adsorption.

It was also noted that coatings with smooth polysiloxane surface had many more barnacles, covering an estimated 10% of the surface, but almost no algae (Fig. 5). Untreated control panels immersed during this same period were colonized by macroalgae ($\approx 50\%$), tubeworms ($>50\%$), bryozoans ($\approx 5\%$), barnacles ($\approx 50\%$) and ascidians ($\approx 20\%$).

After 2 months, surfaces of both samples were more heavily fouled by macroalgae (10–20%), barnacles (5–10%),

![Rough polysiloxane surface](image1)
![Smooth polysiloxane surface](image2)

Fig. 4. AFM of a rough polysiloxane surface.

Fig. 5. Field-trial (after 1 months) results.
and bryozoans (50–60%). The net barnacle population on test surfaces remained less than that on the inert control plates. The results indicate that the superhydrophobic coatings did influence macrofouling colonization but their application for long-term anti-fouling needs further investigation.

4. Conclusions

Superhydrophobic surfaces delay fouling occurrence. For a short period exposure to fouling environments, superhydrophobic surface showed excellent fouling repellency while the hydrophobic film was stained by a large amount of micro-organisms. However, after a long period exposure to seawater, both films lose anti-fouling properties. This is clearly associated with the strength of air bubble adsorption and further studies on the geometry of bubble capture are required.

Nevertheless superhydrophobic coatings show promise for short-term anti-fouling application with no detrimental side effects that are common in poison based formulations.

Acknowledgements

The present research is funded by Faculty Research Grants Program (FRGP 2004) of University of New South Wales, Sydney, Australia.

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