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NANOSTRUCTURED COATINGS FOR RESISTANCE TO AQUATIC BIOFOULING

P. Navabpour, X. Zhang and K. Cooke

Teer Coatings Ltd, Miba Coating Group, West Stone House, Berry Hill Industrial Estate, Droitwich WR9 9AS, UK
(Email:parnia.navabpour@miba.com)

ABSTRACT:

Thin film coatings have been developed to reduce the build-up and to facilitate the removal of biological organisms from aquatic surfaces, using industrially compatible vacuum deposition processes. The aim was to develop coatings which reduce biofouling through their composition and nanostructure rather than the release of toxic biocides, together with good adhesion, and resistance to environmental degradation. The coatings ranged from transparent silicon oxide and siloxanes to double-layer and multilayer coatings. The biofouling evaluated in laboratory tests using the freshwater bacterium, *Pseudomonas Fluorescens* showed significantly improved antifouling performance compared to uncoated and standard surfaces. In addition to their antibiofouling properties, the coatings impart improved mechanical resistance and have the potential for use in a variety of applications, including heat exchangers, sensors and windows for optical and ultrasonic radiation, and filtration membranes. The magnetron sputtering, plasma assisted chemical vapour deposition (PACVD) and hybrid process technology is described and its relevance for anti-fouling applications in heat exchangers is discussed.

INTRODUCTION:

Biofouling has major detrimental effects on a number of applications such as shipping, heat exchangers and oceanographic instruments. In heat exchangers, biofouling results in a reduction in heat transfer rates and an overall loss in efficiency at great cost to the economy (Müller-Steinhagen, 2010). In oceanographic instruments, biofouling leads to the loss of transparency in the optical windows, requiring frequent cleaning and costly maintenance (Davis *et al.*, 1997; Li *et al.*, 2012).

Different approaches are used to address biofouling. One approach involves the use of antifouling formulations where the settlement of the fouling organisms is prevented, typically through the release of biocides. Other less environmentally damaging approaches make use of fouling release coatings and biomimetic structures, where the biological organisms are weakly attached to the coating and are easily detached through the application of hydrodynamic forces (Chambers *et al.*, 2006).

With the introduction of environmental restrictions on biocides (e.g. the EC's Biocidal Products Directive 98/8/CE) the emphasis of the technological development is on coatings which can prevent or reduce the attachment of fouling organisms through the physicochemical properties of the coatings rather than the release of biocides.

This paper presents a review of the results obtained from a series of siloxane coatings deposited at Teer Coatings Ltd. using plasma assisted chemical vapour deposition (PACVD) and a modified process including magnetron sputtering. The effect of coating composition on the antifouling properties as well as the mechanical properties of the coatings has been investigated, with the aim of developing antifouling coatings which are robust enough to withstand real world end use conditions.

EXPERIMENTAL

Coating Preparation

Hexamethyldisiloxane (HMDSO) at 98+% purity was supplied by Sigma–Aldrich, acetone at 99.5% purity by Hammond Chemicals Ltd. Oxygen, argon and nitrogen (99.999%purity) were supplied by BOC. Borosilicate glass slides (76 mm × 26 mm × 1.2 mm) were supplied by VWR International Ltd. Stainless steel 304 slides (76 mm × 26 mm × 1.2 mm) with a 2B finish were supplied by Outokumpu. The description of the coating apparatus is given in detail elsewhere (Akesso *et al.*, 2009; Navabpour *et al.*, 2010). The substrates were placed in the coating chamber using one of two configurations: horizontally on a plate electrode (Akesso *et al.*, 2009) or vertically, facing the magnetrons (Navabpour *et al.*, 2010). Immediately prior to the deposition, slides were cleaned using acetone by immersion in an ultrasonic bath for 15 min. They were then wiped with a fibre-free tissue and were transferred to the PACVD chamber. A maximum of 45

slides was arranged regularly on the substrate holder. Glass substrates were ion cleaned in the chamber in order to prepare them for the coating deposition. The vacuum chamber was evacuated to 1.0×10^{-5} mbar and partially filled with a flow of argon and oxygen (or nitrogen). RF power (13.56 MHz) was supplied to the upper electrode and the lower stainless steel plate electrode. The substrates were treated for 5 – 30 min. The chamber was evacuated to 5.5×10^{-5} mbar prior to commencing coating deposition. The reactive gas comprising O_2 and HMDSO was introduced at a pressure of 0.006 – 0.18 mbar. Plasma was induced by application of power to the RF electrodes. The duration of plasma deposition was varied in order to obtain 1-μm thick coatings. At the end of the coating process, the chamber was evacuated to a pressure of 5×10^{-5} mbar before being returned to atmospheric pressure with ambient air.

Hybrid coatings were produced by simultaneous PACVD and magnetron sputtering from a silicon target. The procedure has been described elsewhere (Navabpour *et al.*, 2010). Prior to the deposition of coatings, substrates were plasma ion cleaned using an RF bias and argon as the working gas. Next a thin layer of silicon was deposited from the silicon target by applying a pulsed-DC current to the magnetron. This stage was followed by the addition of oxygen to generate a gradient SiO_x layer. HMDSO was then added to the system, slowly increasing its flow at the same time as reducing the argon flow. Deposition times were adjusted to give a total coating thickness of around 1μm. Table 1 shows the parameters used for the deposition of the coatings.

Two coatings were deposited from a mixture of HMDSO and N_2 in order to obtain coatings with lower surface energies. The coating deposition procedure was similar to that of HMDSO/O_2 coatings with the horizontal configuration. The only differences were that a higher pressure of 0.5 mbar was applied during deposition and N_2 was used instead of O_2. Table 2 shows the parameters used for the deposition of these coatings.

Characterisation of coatings

Contact angle and surface energy. Contact angle measurements were carried out at room temperature using an advancing angle method with an in-house contact angle analyser. Three test liquids: deionised water, ethylene glycol (Sigma-Aldrich) and diiodomethane (Sigma-Aldrich) were used. Six contact angle measurements were performed for each liquid and the reported values are mean ± 2σ. Surface free energies of the coatings and their dispersive and polar components were calculated using the van Oss acid–base (AB) approach (van Oss, 1994). According to the van Oss approach, surface energy (γ), is seen as the sum of a Lifshitz–van der Waals apolar component γ^{LW} and a Lewis acid–base polar component γ^{AB} ($\gamma^{Tot} = \gamma^{LW} + \gamma^{AB}$). The acid–base polar component γ^{AB} can be further subdivided by using specific terms for an electron donor (γ^-) and an electron acceptor (γ^+)

Table 1 The parameters used for the deposition of HMDSO/O_2 and hybrid coatings

Coating code	Ion cleaning (min)	Reactive gas (sccm)		Deposition (min)	RF bias (W)	RF electrode (W)	Pressure (mbar)	Config.	Si current (A)
		O_2	HMDSO						
Horizontal configuration:									
H06	5	50	6	30	125	200	0.100	H	0
H22	5	50	22	30	125	200	0.100	H	0
H36	5	50	36	20	125	200	0.100	H	0
H36-2	20	50	36	20	125	200	0.100	H	0
Vertical configuration:									
V125	20	19	16	70	125	0	0.003	V	0
V100	20	19	16	100	100	0	0.003	V	0
V50	20	19	16	100	50	0	0.003	V	0
Hybrid1	20	19	16	40	50	0	0.003	V	3
Hybrid2	20	23	12	50	50	0	0.003	V	3
Hybrid3	20	27	8	100	50	0	0.003	V	3

Table 2 Parameters used for the deposition of HMDSO/N_2 coatings

Coating code	Ion cleaning time (min)	HMDSO (sccm)	N_2 (sccm)	Deposition time (min)	RF bias (W)
N45	20	36	45	20	125
N95	20	36	95	20	125

subcomponent, where

$$\gamma^{AB} = 2\sqrt{\gamma^{-}\gamma^{+}}$$

Hardness measurements. Hardness measurements were performed on films deposited onto glass substrates using a Fischerscope™ HM2000 micro-indentation system from Fischer Technology, Inc. Tests were carried out with a Vickers diamond indenter with loads from 0.4 to 10 mN. During the penetration of the test surface by the indenter under load, hardness and modulus can be determined from the resultant load vs indentation depth curve (loading/unloading) which gives the value of composite hardness (comprising effects from both the coating and the substrate) and an effective modulus $E^* = E/(1-\nu^2)$ where E = elastic modulus and ν = Poisson's ratio. The hardness reported here is HUplast which is based on the lasting indentation after unloading. At least five indentation cycles were performed to create a mean value graph from which calculations were derived. The values reported for hardness and modulus are mean ± 2σ.

Scratch resistance. The scratch and wear resistance of the coatings were assessed using a Teer ST3001 scratch–wear tester. The coatings deposited on glass substrates were assessed using a 1.5-mm diameter tungsten carbide ball while coatings deposited on a hardened (HRc 64) M42 high-speed steel were evaluated using a Rockwell diamond tip (radius 200μm). A load rate of 100 N min $^{-1}$ and a constant sliding speed of 10.0 mm min^{-1} were used with the load increasing from 10 to 40 N.

Attachment and adhesion of freshwater bacteria. The method for the evaluation of attachment and adhesion of the freshwater bacteria *Pseudomonas Fluorescens* has been described in detail elsewhere (Akesso *et al.*, 2009). In brief, the samples were immersed in a glass tank containing a suspension of *P. Fluorescens* and incubated at 28°C for 1 h. The samples were removed and dipped twice vertically in sterile distilled water under a constant speed. To assess the adhesion strength of attached bacteria, samples were dipped 20 times vertically in a glass tank containing sterile distilled water at 28°C under constant shear stress. Samples were transferred to a second glass tank containing sterile distilled water at 28°C and sonicated in an ultrasonic bath to remove all the remaining attached bacteria. The numbers of bacteria detached by the two procedures were determined. Aliquots of water from both tanks were plated into standard Petri dishes containing agar and incubated for 24 h at 28°C. The total number of bacteria attached to the sample and the percentage removal were calculated.

RESULTS AND DISCUSSION

The effect of various coating parameters on the mechanical properties of the coatings is shown in Figure 1.

As can be seen, increasing the HMDSO/O_2 ratio results in a reduction in the hardness and modulus of the coatings whilst increasing the RF power and the amount of sputtered silicon lead to an increase in these properties. Figure 2 shows scratch tracks on coatings deposited on glass and Figure 3 shows scratch tracks on coatings deposited on M42 high-speed steel without and with a silicon adhesion layer and sputtered silicon content in the PACVD coating. It can be seen that the addition of the sputtered silicon considerably improves the adhesion and the robustness of the coatings.

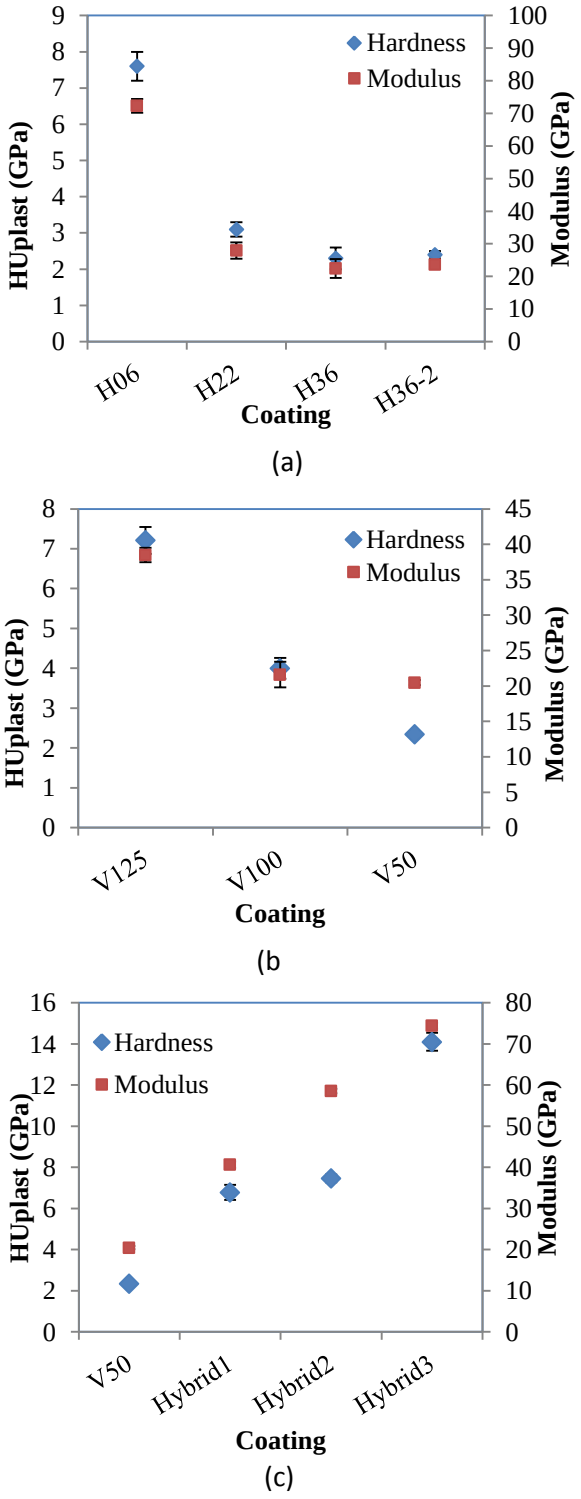


Figure 1 The effect of (a) HMDSO/O_2 ratio, (b) RF power and (c) sputtered silicon on the hardness and the effective modulus (E^*) of the coatings

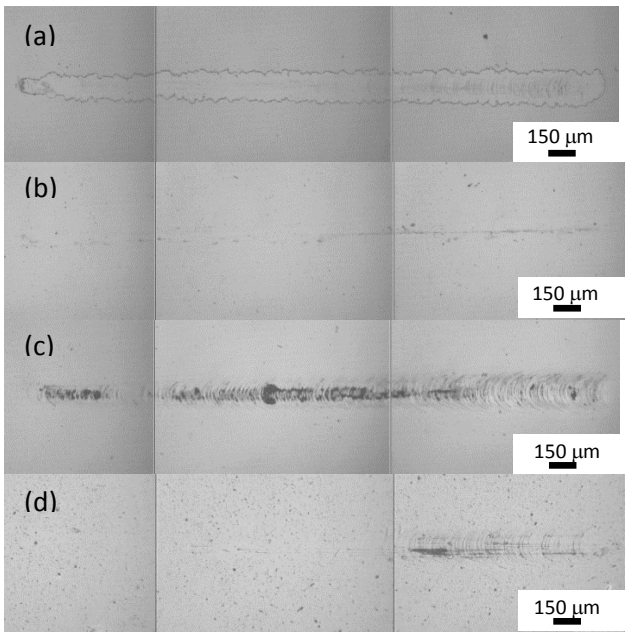


Figure 2 Scratch tracks on coatings deposited on glass (a) V50, (B) Hybrid1, (C) Hybrid2, (D) Hybrid3 (Navabpour *et al.*, 2010)

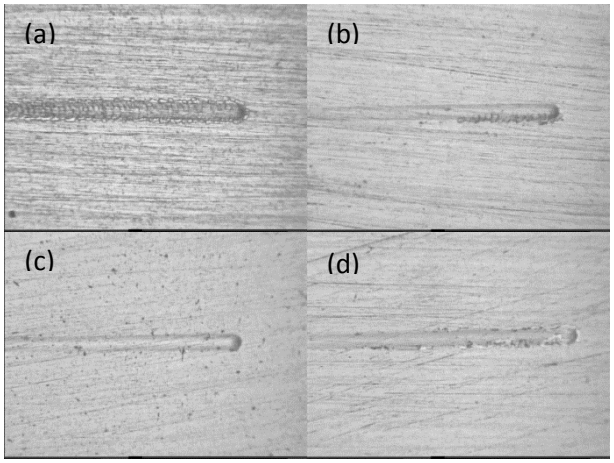


Figure 3 Scratch tracks on coatings deposited on M42 steel (a) V50, (B) Hybrid1, (C) Hybrid2, (D) Hybrid3 (Navabpour *et al.*, 2010)

The effect of wettability and surface energy on antifouling and fouling release properties has been widely investigated. Both hydrophobic (Fletcher and Loeb, 1979) and hydrophilic (Chen *et al.*, 2006) antibiofouling surfaces have been reported. The positive effect of a low surface energy on antifouling properties has been reported in several papers, such as (Chambers *et al.*, 2006). A review by Callow and Callow (2011) summarises some of the mechanisms through which antifouling properties are achieved and shows that these properties are highly species-dependent.

The surface energy of the coatings is shown in Table 3. Figure 4 and 5 show the effect of HMDSO content and added sputtered silicon in the PACVD coatings on the attachment and removal of the freshwater bacteria, *Pseudomonas Fluorescens.* It can be seen that there was a direct relationship between the bacterial attachment with the surface energy and the siloxane coatings with lower surface energy showed better antifouling properties. The effect of surface energy on the removal was less clear due to the larger measurement errors in the data. An increase in the removal was, however, evident in samples with significantly lower surface energies.

Table 3 Surface energy of the coatings

Coating code	**Surface energy (mN m^{-1})**			
	γ^{LW}	γ	γ^{-}	γ^{Total}
H06	29.60	1.64	39.50	45.7
H22	24.30	0.16	8.30	26.6
H36	23.30	0.04	6.40	24.30
H36-2	22.60	0.01	4.70	23.10
V125	29.49	0.002	0.6	29.56
V100	29.09	0.06	0.76	29.5
V50	23.38	0.07	1.5	24.04
Hybrid1	25.65	0.14	1.65	26.61
Hybrid2	24.96	0.02	1.33	26.05
Hybrid3	27.6	0.76	14	34.13

This suggests that coatings with lower surface energies than the above may have even better antifouling properties. Coatings deposited from a mixture of HMDSO and nitrogen have been reported to have very low surface energies (Michaeli *et al.*, 2012).

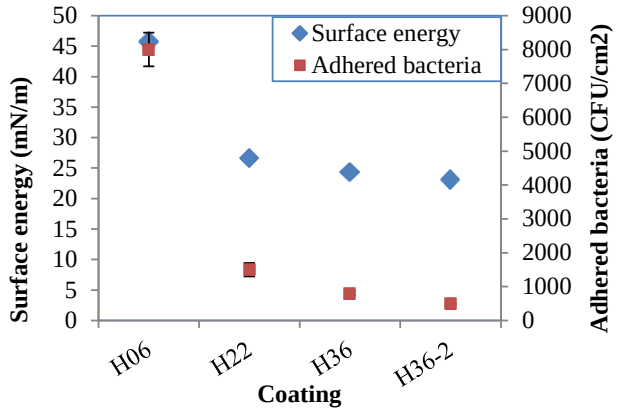
The effect of nitrogen on the contact angle and surface energy has been summarised in Table 4. Whilst coatings deposited from HMDSO/O_2 had a water contact angle in the range 40 – 94°, the water contact angle on HMDSO/N_2 coatings reached 121°. The contact angle increased further to 150° through changing the surface structure, achieved by the deposition of a multi-layer coating with a titanium first layer, followed by a gradient nanostructured titanium oxynitride layer and finally HMDSO/N_2 (see Figure 6).

In addition to their antifouling properties, the coatings presented in this work can lead to a number of other benefits. The PACVD siloxane coatings are transparent and are hence suitable for applications where transparency is required, e.g. on optical windows. A preliminary evaluation of the coatings for heat exchanger applications showed that the presence of coatings does not have a negative effect on the heat transfer rate of the plates. Furthermore, hydrophobic coatings have been shown to aid drop-wise condensation, which can potentially result in improved heat transfer rates (Lara and Holtzapple, 2011). The deposition of a double-layer coating with silicon or titanium base layer can impart enhanced corrosion resistance, making it possible to use less noble and less expensive materials for heat exchangers.

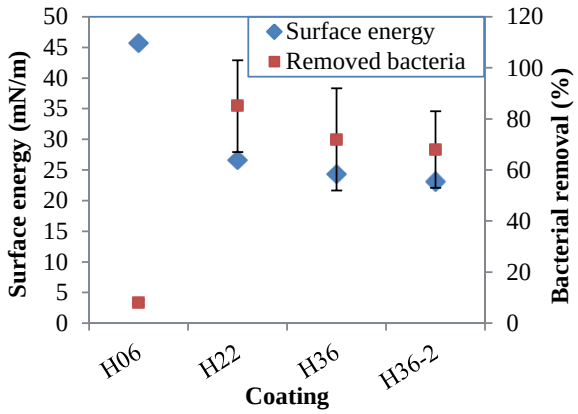
The deposition technology developed in this research, a hybrid combination of PACVD and reactive magnetron sputtering, is eminently scalable, since the individual techniques are already industrially applied in, for example, the PACVD web coating of packing films and the reactive magnetron sputtering of

Table 4 Contact angle and surface energy of coatings deposited using HMDSO and N_2.

	Contact angle (°)			Surface energy (mN/m)			
Coating	**Water**	**Diiodomethane**	**Ethylene glycol**	γ^{LW}	γ	γ^{-}	γ^{Total}
N45	117.3 ± 2.6	84.7 ± 1.9	101.0 ± 2.7	15.16	0.13	0.43	15.63
N95	121.8 ± 3.4	86.0 ± 3.6	108.2 ± 2.2	14.55	0.36	0.50	15.40

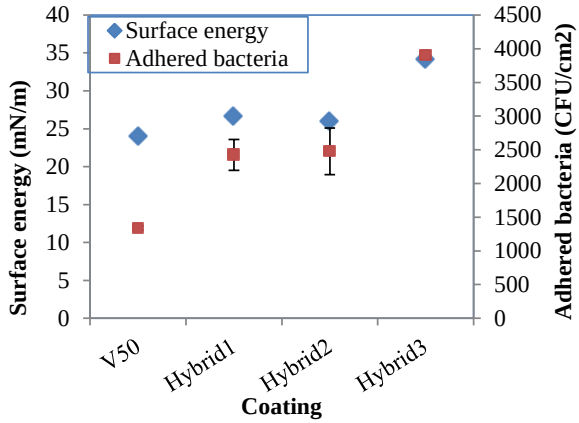


(a)

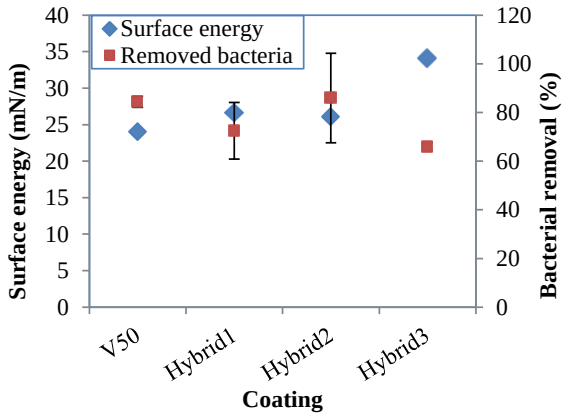


(b)

Figure 4 The effect of HMDSO content on (a) Bacterial attachment and (b) removal (Akesso *et al.*, 2009-2).



(a)



(b)

Figure 5 (a) Bacterial attachment and (b) removal for Hybrid coatings. V50 is also given for comparison (Navabpour *et al.*, 2010)

architectural glass panels. The productivity of the existing batch process could be transformed, for example by the introduction of in-line air to vacuum load-locks to enable the semi-continuous processing of suitable components. The performance of the coating under high temperatures for extended periods needs to be established and is the subject for a further study.

CONCLUSIONS

Plasma-assisted chemical vapour deposition (PACVD) siloxane coatings from a mixture of hexamethyldisiloxane (HMDSO) and O_2, and hybrid coatings deposited by simultaneous sputtering of silicon and plasma polymerisation of HMDSO+O_2 were prepared on glass and steel substrates. The mechanical properties, surface energy and fouling and removal (cleaning) behaviour of the coatings were evaluated. Surface energy was found to play an important part in the fouling resistance of the coatings. Mechanical properties were improved by the deposition of silicon from a magnetron target and by the addition of the reactive gas. Siloxane coatings did not adversely affect the heat transfer rate of the heat exchanger plates and the use of a titanium base layer resulted in improved corrosion resistance. Coatings with lower surface energies were deposited from a HMDSO/N_2 reactive gas mixture and by using nanostructured surfaces which could improve the fouling resistance even further. The hybrid deposition process described here is industrially compatible and eminently scalable to meet future commercial requirements.

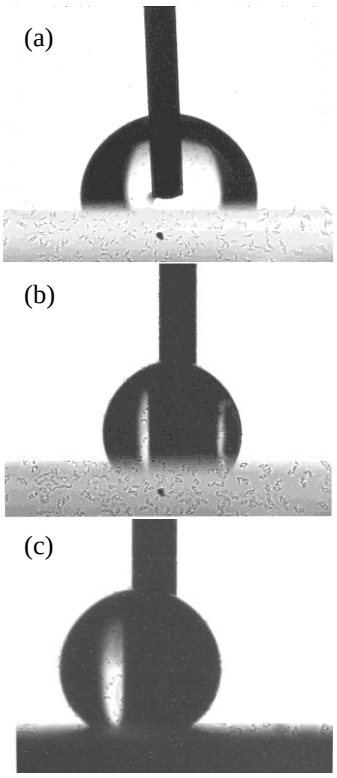


Figure 6 Water contact angle on (a) H36-2, (b) N95 and (c) TiON-N95 double layer coating

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