Biofouling
The Journal of Bioadhesion and Biofilm Research
Publication details, including instructions for authors and subscription information:
http://www-intra.informaworld.com/smpp/title~content=t713454511

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First Published on: 20 May 2008

To cite this Article: Beigbeder, Alexandre, Degee, Philippe, Conlan, Sheelagh L., Mutton, Robert J., Clare, Anthony S., Pettitt, Michala E., Callow, Maureen E., Callow, James A. and Dubois, Philippe (2008) 'Preparation and characterisation of silicone-based coatings filled with carbon nanotubes and natural sepiolite and their application as marine fouling-release coatings', Biofouling, 24:4, 291 — 302

To link to this article: DOI: 10.1080/08927010802162885
URL: http://dx.doi.org/10.1080/08927010802162885

Biofouling
Vol. 24, No. 4, July 2008, 291–302

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Preparation and characterisation of silicone-based coatings filled with carbon nanotubes and natural sepiolite and their application as marine fouling-release coatings

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(*Received 26 February 2008; final version received 24 April 2008*)

This article reports on the preparation and partial characterisation of silicone-based coatings filled with low levels of either synthetic multiwall carbon nanotubes (MWCNTs) or natural sepiolite (NS). The antifouling and fouling-release properties of these coatings were explored through laboratory assays involving representative soft-fouling (*Ulva*) and hard-fouling (*Balanus)* organisms. The bulk mechanical properties of the coatings appeared unchanged by the addition of low amounts of filler, in contrast to the surface properties, which were modified on exposure to water. The release of *Ulva* sporelings (young plants) was improved by the addition of low amounts of both NS and MWCNTs. The most profound effect recorded was the significant reduction of adhesion strength of adult barnacles growing on a silicone elastomer containing a small amount (0.05%) of MWCNTs. All the data indicate that independent of the bulk properties, the surface properties affect settlement, and more particularly, the fouling-release behaviour, of the filled materials.

Keywords: algae; barnacles; carbon nanotubes; fouling-release coatings; nanocomposite; sepiolite; silicones

Introduction

Biofouling presents important technical, scientific and economic challenges to marine industries. Fouling on ships' hulls decreases speed and manoeuvrability and also increases propulsive fuel consumption (Townsin 2003). Slime films can lead to significant increases in resistance and powering, and heavy, hard (calcareous) fouling can result in powering penalties up to 86% at cruising speed (Schultz 2007). Until recently, fouling was primarily controlled by paints containing tributyltin (eg Jelic-Mrcelic et al. 2006) and while biocidal antifouling (AF) paints still dominate the AF market, there is pressure on the marine industry to promote the development of non-biocidal alternatives.

Several environmentally benign strategies to control fouling have been proposed including natural compounds (Clare 1996; Fusetani 2004), enzymes (Olsen et al. 2007) and a variety of physical and/or topographical surface designs that deter the settlement of the colonising cells or larvae and/or reduce adhesion (Genzer and Effimenko 2006; Schumacher et al. 2007a,b). A number of systems based on a large range of polymeric materials including polyurethanes, fluoropolyurethanes or other perfluoropolymers have shown adhesion resistance (Bultman and Griffith 1994; Schmidt et al. 2004). However, the most promising coatings are based on silicone elastomers. These 'fouling-release' (FR) coatings promote the release of the accumulated fouling as a result of the hydrodynamic forces generated by movement through the water (Swain 1999; Schultz et al. 2003; Kavanagh et al. 2005). The basis of low adhesion is attributed to a number of factors including low surface energy (Brady and Singer 2000) and low glass transition temperature (Patwardhan et al. 2006), the latter resulting in high local chain mobility. Other parameters also contribute to the release of attached 'hard'-fouling organisms such as barnacles and tubeworms, including the bulk modulus (Brady and Singer 2000; Singer et al. 2000; Berglin et al. 2003; Stein et al. 2003; Kim et al. 2007) and the thickness of the coating (Brady and Singer 2000; Wendt et al. 2006). These parameters are also important for the release of 'soft'-fouling organisms such as algae (Chaudhury et al. 2005).

Although coatings based on silicone elastomers have inherently good FR properties, they also suffer from the disadvantage of being mechanically weak and

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ISSN 0892-7014 print/ISSN 1029-2454 online

DOI: 10.1080/08927010802162885
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therefore easily damaged, which limits their practical use. One strategy to overcome this drawback is to insert fillers into the polymeric matrix to create a composite material, the challenge being to incorporate mechanical reinforcement without detriment to the FR properties. In the last few years polymer-based nanocomposites incorporating nano-sized fillers have been extensively investigated (Alexandre and Dubois 2000, Schmidt et al. 2002). The merits of this approach are that the nano-sized particles provide a larger interface for interactions with the polymer matrix leading to potentially improved properties. Such materials have been extensively investigated for their electrical (Chatterjee et al. 2006), flame-retardant (Beyer 2002) and optical (de Paiva et al. 2007) properties and show promise for application in relevant industries, but as yet there has been little published effort on this approach for marine coatings. Controlling or designing surfaces at the nano-level makes it possible to develop new types of coatings with targeted properties. As a simple example it is well known that the nanostructuring of a surface can alter the wetting properties (''Lotus effect'') leading to self-cleaning or superhydrophobic coatings (see Genzer and Efimenko 2006; Marmur 2006). In the case of PDMS materials, various methods have been developed such as CO_2-pulsed lasers (Khorazani et al. 2005), laser etching (Jin et al. 2005) or nanocasting (Sun et al. 2005), but as far as is known, the use of nanofillers has not been investigated systematically. With this in mind, this article reports on the preparation and partial characterisation of novel silicone-based coatings filled with a low level of either synthetic multiwall carbon nanotubes (MWCNTs) or natural sepiolite (NS). The wettability of the nanofilled silicone-based coatings, before and after immersion, their cross-linking density (ie swelling behaviour) and their elastic modulus are reported and discussed. The AF and FR properties of these coatings were explored through laboratory assays involving representative soft-fouling (*Ulva*) and hard-fouling (*Balanus)* organisms.

Natural sepiolite (NS) is a microcrystalline-hydrated magnesium silicate with $Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4{\cdot}8H_2O$ as the unit cell formula. It exhibits a microfibrous morphology with a particle thickness and width of ca. 10–30 nm and length typically from 2 to 5 μm. Structurally, NS is formed by an alternation of blocks and tunnels, which grow up in the fibre direction. Generally, NS needles are assembled in bundles of aggregated fibres. As a consequence of its structural morphology, NS has received considerable attention regarding its use as a reinforcement nanofiller within polymeric matrices (Bokobza 2004; Chen et al. 2007; Ma et al. 2007).

Carbon nanotubes (CNTs) have been studied intensively since their discovery in 1991 (Iijima 1991). Their structure is built up of carbon atoms arranged in hexagons and pentagons, forming cylinders with diameters from 2 to 30 nm and length that can be in the micron range. Usually, CNTs consist of single-walled or multi-walled nanotubes where several nanotubes of decreasing diameter are interlocked. Because of their excellent physical, mechanical properties and high aspect ratios (Tai et al. 2004; Yaobang et al. 2004; Bokobza and Kolodziej 2006) they also appear as candidates of choice for the reinforcement of polymeric materials.

Ulva (syn. *Enteromorpha*) is the most common macroalga that fouls ships and other submerged structures. Dispersal is mainly through motile, quadriflagellate zoospores (approximately 7–8 μm in length), which are released in large numbers and form the starting point of the assay (Callow et al. 1997). The swimming spores settle and adhere through discharge of a glycoprotein adhesive (Callow and Callow 2006) then rapidly germinate into sporelings (young plants), which adhere weakly to silicone FR coatings (Chaudhury et al. 2005; Cassé et al. 2007a,b). The barnacle, *Balanus amphitrite* (Clare and Høeg 2008) is cosmopolitan in its distribution and an economically important fouling species. The adults, which are hermaphrodite, liberate nauplii that develop through six planktonic stages to the highly specialised settlement stage, the cypris larva (Clare and Matsumura 2000). The cyprid explores surfaces using a reversible adhesion mechanism. Once a suitable site for settlement has been located, permanent cement is discharged that anchors the larva in place during metamorphosis and early juvenile development (Phang et al. 2006). Subsequently, adult cement is produced periodically as the barnacle grows. Both the cyprid and adult adhere weakly to fouling-release coatings, but only the latter has been studied with regard to factors that contribute to easy release.

Materials and methods

Materials

Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) was used as the silicone elastomer. The formulation consists of two parts, A and B, which are mixed together in a ratio of 10:1 in order to obtain a cross-linked PDMS via hydrosilylation. The natural sepiolite (NS) was purchased from Tolza (Spain). The multiwall carbon nanotubes (MWCNTs) were kindly provided by Nanocyl S.A. Belgium (commercial grade 7000). The properties of both nanofillers, supplied by manufacturers, are summarised in Table 1 and representative images obtained by transmission electronic microscopy are shown in Figures 1 and 2.

Table 1. Properties of natural sepiolite (NS) and multi-wall carbon nanotubes (MWCNTs), as supplied by the manufacturers.

Property (unit)	NS	MWCNTs
Average diameter (nm)	10–30	10
Length (μm)	2–5	0.1–10
Carbon purity (%)	–	90

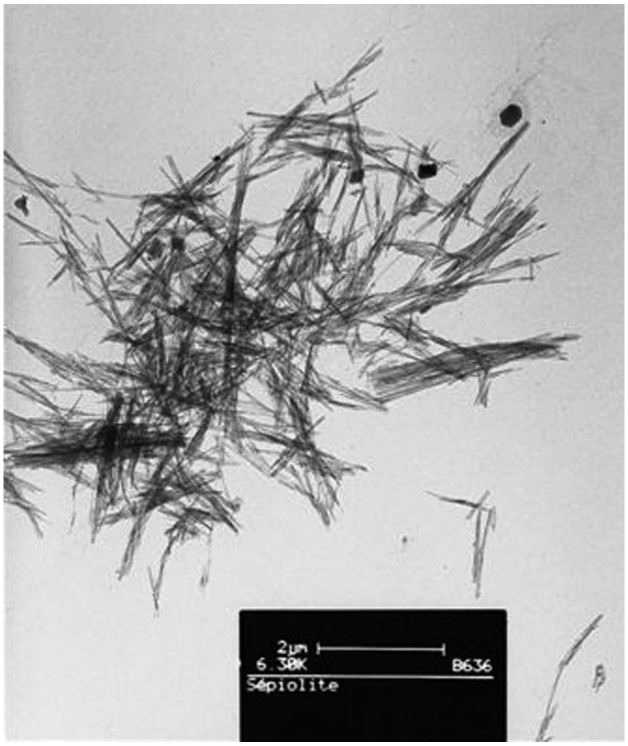

Figure 1. TEM image of natural sepiolite (NS). Scale bar = 2 μm.

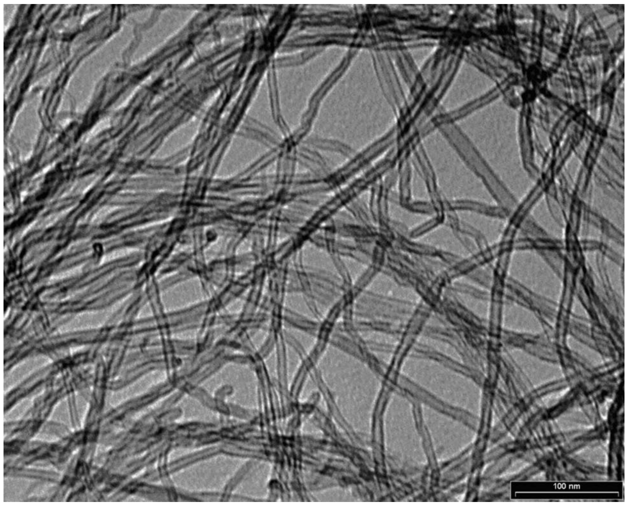

Figure 2. TEM image of multiwalled carbon nanotubes (MWCNTs), grade 7000, Nanocyl. Scale bar = 100 nm.

PDMS (part A) and MWCNTs or/and NS were mechanically mixed (1200 rpm for 2.5 h for MWCNTs; 1000 rpm for 0.5h for NS). When both fillers were added, the MWCNTs were firstly mixed (1200 rpm for 2.5 h) followed by NS (1000 rpm for 1 h). Then part B was added and the mixture stirred at 500 rpm for 1 min. Glass slides, pre-treated with a silane coupling agent (Primer OS1200; Dow Corning), were fixed to a mould and the mixture was applied. Addition of fillers in the silicone contributes to an increase the viscosity in such a way that transferring the silicone mixture into the mould required the use of a foam paint brush to obtain a surface as flat as possible. After 30 min at room temperature and 8 h at 105°C, coatings with a thickness of 200–300 μm were obtained. Within a specific experiment, coatings of uniform thickness were used (see later).

Dynamic mechanical analyses

The dynamic mechanical properties of the samples were analysed at room temperature with a dynamic mechanical analyser DMA (TA Instrument 2980) operating in tensile strain-sweep mode. A frequency of 1 Hz, a preload of 0.1 N and amplitude from 0.5 to 27 μm were used. The tensile moduli are the results of an average of at least four measurements. The standard deviations (SDs) are shown as the error bars (Figure 3).

Tensile tests

The tensile tests were carried out using a Lloyd LR 10 K tensile tester (ASTM 638 type V norm) at room temperature. The gauge length was set as 25.4 mm and the deformation speed at 20 mm/min. The values reported here represent an average of the results for

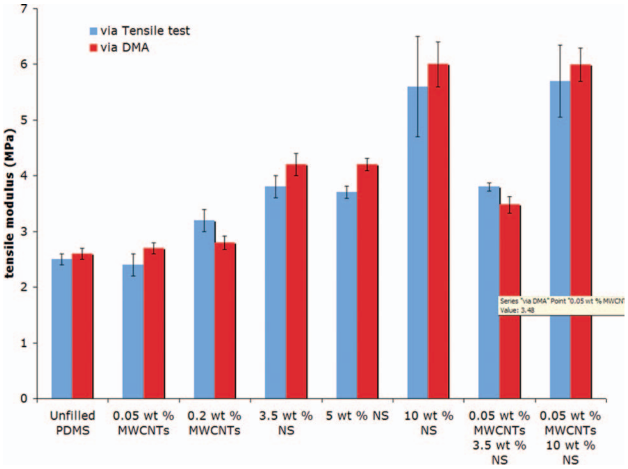

Figure 3. Tensile moduli of MWCNT and NS-filled PDMS as determined by tensile tests and DMA. Bars = SD.

tests run on at least six specimens. The SDs are shown as error bars (Figures 3 and 4).

Swelling measurements

For the swelling tests, rectangular pieces of elastomer (1 cm × 1 cm × 0.5 cm) were immersed in 100 ml of heptane for 24 h. The solution was renewed every 3 h during the first 10 h. The samples were dried overnight at 70°C under vacuum. Each point recorded is the mean of three samples and the reported values (100% of polymer) take account of the mass fraction of filler. The swelling degree S was calculated in grams of solution per gram of dry polymer at a time t, as:

$$S(t) = \frac{w_t - w_0}{w_0} \times 100\%. \tag{1}$$

where w_t was the weight of the sample at t and w_0 the weight of the dried sample. S was determined at 25°C.

Contact angle measurements

Static contact angle measurements were performed on nanofilled silicone-coated microscopic slides using a Kruss DSA 10 apparatus and the sessile drop technique. The hydrophobic/hydrophilic character of the PDMS layer was evaluated by measuring the contact angle between the surface of the coating and drops of demineralised water (50 μl). The results are the mean of a minimum of five determinations.

Biological assays

Coated slides were immersed in racks placed in 30 l tanks of deionised water that were continuously circulated through a carbon filter for 7 days. Samples were equilibrated in artificial seawater (ASW) for 1 h before the start of the assays.

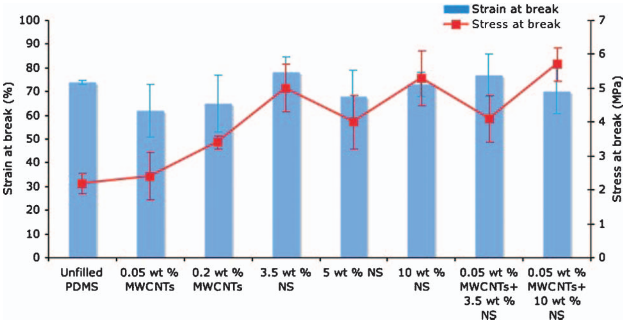

Figure 4. Stress and strain at break of MWCNT and NS-filled PDMS as determined by tensile tests. Bars = SD.

Zoospore settlement and strength of attachment

Zoospores of the green macroalga *Ulva linza* were released from reproductive thalli into artificial seawater (ASW) at pH 8.0 and 32 ‰ ('Tropic Marin', Aquarientechnik GmbH). A suspension containing 1.5 × 10^6 zoospores/ml was used for settlement assays following the principles outlined in Callow et al. (1997). In brief, each surface was placed in a separate compartment of a Quadriperm dish (Greiner Bio-one Ltd) to which 10 ml of zoospore suspension were added. Zoospores were allowed to settle for 45 min in the dark, before the residual suspension was aspirated and the slides washed to remove unsettled (swimming) spores. Three replicates of each coating were used to obtain a spore count prior to exposure to flow and three replicates were exposed for 5 min to hydrodynamic forces generated in a flow channel that produced a wall shear stress of 52 Pa. The flow channel produced fully developed turbulent flow similar to that experienced around the hull of a ship travelling at 15 knots (Schultz et al. 2000). Slides were fixed in 2.5% (v/v) glutaraldehyde, washed and air-dried as described in Callow et al. (1997). The density of settled (adhered) spores was determined using a Zeiss Kontron 3000 image analysis system attached to a Zeiss epifluorescence microscope and video camera as described in Callow et al. (2002). Thirty fields of view, each 0.17 mm^2, were counted at 1 mm intervals along the length of each of three replicates slides. Zoospore removal data are expressed as a percentage of the initial settlement density. Percentage data were arcsine transformed prior to statistical analysis.

Growth and strength of attachment of Ulva *sporelings*

Experiments were also conducted on sporelings, ie young plants that develop from attached spores. Zoospores were allowed to settle for 90 min using a suspension containing 1 × 10^6 spores/ml. After washing, the slides were replaced in Quadriperm dishes to which 10 ml of growth medium were added. Sporelings were grown for 7 days at 18°C with a 16 h:8 h light:dark cycle, prior to the determination of biomass. The medium was refreshed every 2 days. Because samples containing MWCNTs were dark in colour, all dishes were placed on a black background in order to eliminate any effects on growth caused by differential absorption/reflection of light (see Finlay et al. 2008).

Sporeling biomass was measured *in situ* on slides by the autofluorescence of chlorophyll (430 nm/630 nm excitation/emission respectively) using an adapted multi-well plate reader (Tecan Genios Plus). The intensity of emitted light had previously been shown to scale linearly with μg chlorophyll *a* ml^{-1} as determined by DMSO extraction (Jeffrey and

Humphrey 1975). Fluorescence was recorded as Relative Fluorescence Units (RFU) from direct readings. The slides (6 replicates) were read from the top, 216 readings per slide, taken in blocks of 30 × 9.

To assess the strength of adhesion of the sporelings, the slides were exposed to a wall shear stress of 52 Pa in a flow channel as described earlier. Percentage removal of sporeling biomass was determined from the RFU values recorded before and after exposure to flow using 216 paired (before and after) readings per replicate slide. Removal was calculated for each of these individual points in the sporeling biofilm. Percentage removal data were arcsine transformed and the normality assessed using the Anderson-Darling test for conformity. Differences between surfaces were tested using a 1-way ANOVA followed by Tukey's test for pairwise comparisons.

Barnacle cyprid settlement assay

Cypris larvae were cultured according to Hellio et al. (2004) from larvae released from adult broodstock. Assays of settlement inhibition followed standard methodology (eg Hellio et al. 2005), but modified for glass slides contained within the wells of Quadriperm dishes (Greiner Bio-one Ltd). Briefly, this entailed adding 20 × 3-day-old cyprids to each slide contained within 1 ml ASW. The slides were incubated at 28°C for 24 h in the Quadriperm dishes with the lids replaced. Slides were then inspected under a dissecting microscope and settled (permanently attached or metamorphosed) and non-settled individuals were enumerated. Results are expressed as mean percentage settlement.

Adhesion strength of adult barnacles

Approximately 50 × 3-day-old cyprids were introduced to each slide in 1.5 ml ASW. The slides were incubated at 28°C for 48 h in Quadriperm dishes; 0.5 ml dilute ASW was added after 24 h. After this period, algae (75% *Tetraselmis suecica*: 25% *Skeletonema costatum*) were added, *ad libitum*, as a food source for the newly settled barnacles. Juveniles continued to be fed the same algal diet every other day for the first 5–7 weeks and when deemed large enough were moved to the larger grow-on tanks and the feed changed to freshly-hatched nauplii of *Artemia* sp. (Artemia International LLC). The juvenile barnacles were grown on for a period of approximately 3 months, or until the diameter of the majority of their bases measured at least 5 mm. The critical removal stress was measured using a purpose-built barnacle push-off machine (Advanced Analysis and Integration Ltd., Manchester, UK) and adopting the recommendation of ASTM D5618 with respect to the rate of force development. Details of the instrumentation will be reported elsewhere (Conlan et al. personal communication). Briefly, this machine automates measurements of the force required to remove the barnacle from the coating and the basal area. The instrument's software then computes the critical removal stress, which is the force normalised to the barnacles' calcified bases (Wendt et al. 2006). Data for barnacles that had $>10\%$ of their bases remaining attached to the surface after testing were removed from the analysis.

Results

Properties of nanocomposites

The composites filled with various amounts of MWCNTs and NS were characterised by DMA and tensile tests. The tensile moduli of the samples were taken as the slope of the best-fit line to the plots of stress versus strain and the results are shown in Figure 3. Good agreement was found between both methods.

From the results, it appears that tensile modulus is not affected by the incorporation of a small amount of MWCNTs (up to 0.2 wt%) with an average value remaining at 2.6 ± 0.2 MPa. In other words, the stiffness of silicone-based materials remains constant. Swelling measurements were also carried out (Table 2). Such experiments are generally used to estimate cross-linking density, average molecular weight of the polymer between cross-links (Mc) or interaction parameter between polymer and solvent (Zhang et al. 1989; Erva et al. 1998). Percent swelling for the MWCNT-filled PDMS was 90% ± 2% with no significant difference between each loading, attesting to a constant degree of cross-linking.

The decrease of the swelling degree of PDMS in heptane with NS loading is reported in Table 2. Regarding the mechanical properties, the data for the NS-filled PDMS show a progressive increase in the tensile modulus with increased loading (Figure 3).

Table 2. Swelling degrees of the nanofilled silicone-based coatings.

Formulation	Unfilled PDMS	0.05 wt% MWCNTs	0.2 wt% MWCNTs	3.5 wt% NS	10 wt% NS	0.05 wt% MWCNTs + 10 wt% NS
Swelling degree (%)	92 ± 3	88 ± 1.4	88.5 ± 3.5	87.3 ± 2	76.2 ± 0.7	82.4 ± 0.1

The value of 2.6 MPa for the unloaded formulation increased to 6 MPa at 10 wt% loading. The increase in the modulus observed at the higher content of NS (10 wt%) could be due to the presence of aggregates. The addition of both nanofillers does not show any synergistic effect since the value of modulus appears very close to that obtained for the sepiolite-based composite.

Regarding the ultimate properties (Figure 4), no significant modification of the strain at break was detected for the filled PDMS in comparison to the control. In all cases, the elongation at break remained close to 65–75%. For MWCNT-based materials and within the limited content of nanotubes investigated in this study, the stress at break increased from 2.5 to 3.5 MPa (for the higher content in MWCNTs). The effect of NS on stress at break is more pronounced reaching an average value of 5 MPa, but independent of filler content, at least for loading higher than 3.5 wt%.

The surface properties of the coatings were characterised by static contact angle measurements before and after immersion in demineralised water for 7 days (Figure 5a and b). Before immersion, the unfilled PDMS coating had a water drop contact angle of 101° and so exhibited a hydrophobic behaviour. In the presence of nanofillers and before immersion, the wettability of the coatings was not affected with an average value for the contact angle equal to 102° ± 2°. After immersion of the unfilled coating, the contact angle dropped from 101 to 89° indicating a decrease of surface hydrophobicity. After drying, the contact angle reached a value close to that obtained before immersion (Figure 5a). Thus, this surface modification appears to be reversible. In the case of the nanofilled materials, after immersion the static contact angles increased from 89° ± 2° (unfilled PDMS) to 95° ± 3° (average value for the filled PDMS) meaning that the surface became slightly more hydrophobic (Figure 5b).

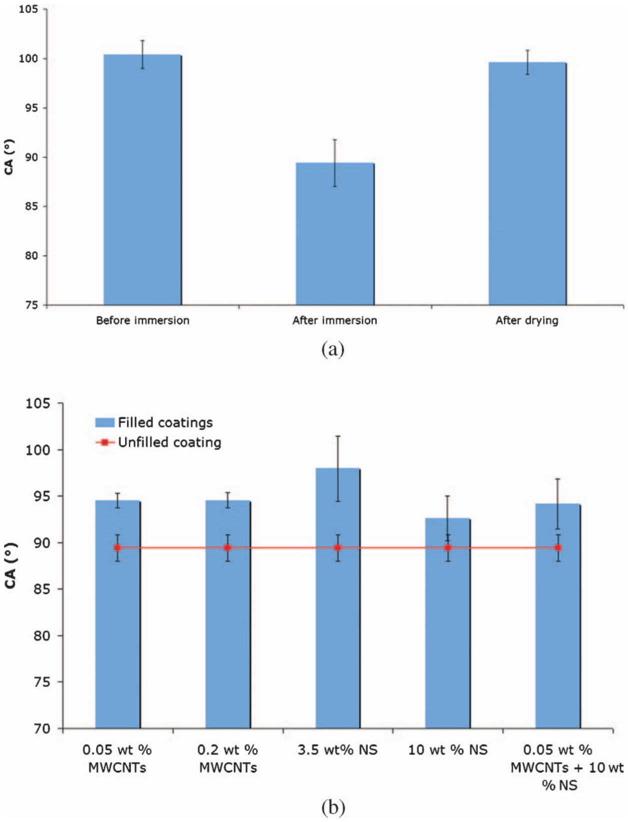

Figure 5. (a) Static contact angle of the unfilled PDMS coating (before immersion, after immersion and after drying). Bars = SD. (b) Static contact angle of the nanofilled silicone-based coatings after immersion. Bars = SD.

Settlement of Ulva *zoospores and strength of attachment*

The addition of NS to the base polymer caused an increase in the number of spores that settled, approximately twice the number being associated with the coating containing 10% NS compared to the unfilled control (Figure 6). The density of settled spores on the coating with 10% NS was significantly different to that on all other coatings ($p < 0.01$).

Between 45 and 65% of the settled spores were removed from all coatings by exposure to a wall shear stress of 52 Pa (Figure 7). Percentage removal from the coatings containing 10% NS and 0.2% MWCNTs was significantly greater ($p < 0.05$) to that from the other coatings including the unfilled control.

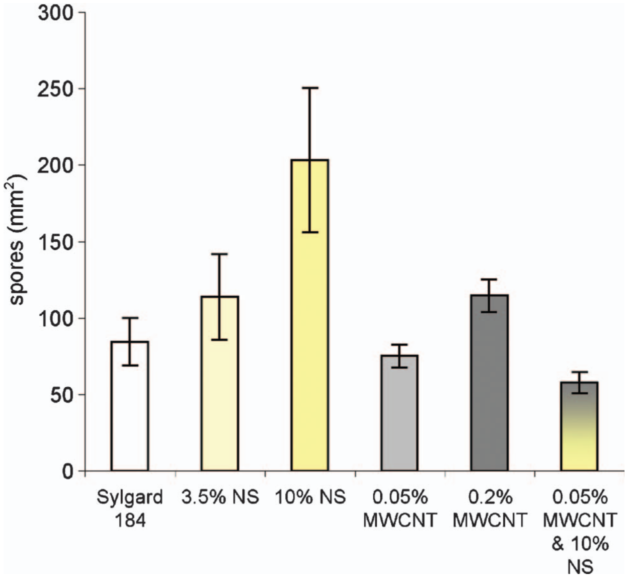

Figure 6. Density of *Ulva* zoospores attached to the unfilled (Sylgard 184) and filled silicones. Each point is the mean of 90 counts, 30 from each of 3 replicates. Bars = 2 × SEM.

Growth and strength of attachment of Ulva *sporelings*

Sporelings (young plants) grew well and a green lawn covered all surfaces after 7 days. The percentage removal of the resulting biomass (Figure 8) was significantly higher from all of the nanofilled silicones compared to the unfilled control ($p < 0.05$).

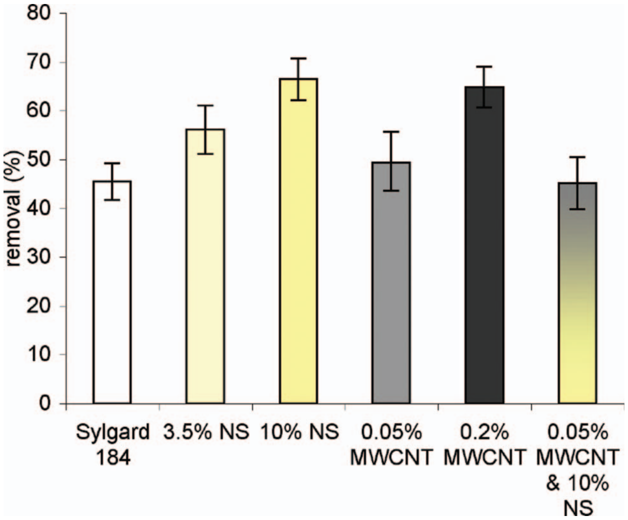

Figure 7. Percentage removal of *Ulva* zoospores from unfilled (Sylgard 184) and nanofilled silicones following exposure to a wall shear stress of 52 Pa. Each point is the mean of 90 values. Bars = 2 × SEM from arcsine-transformed data.

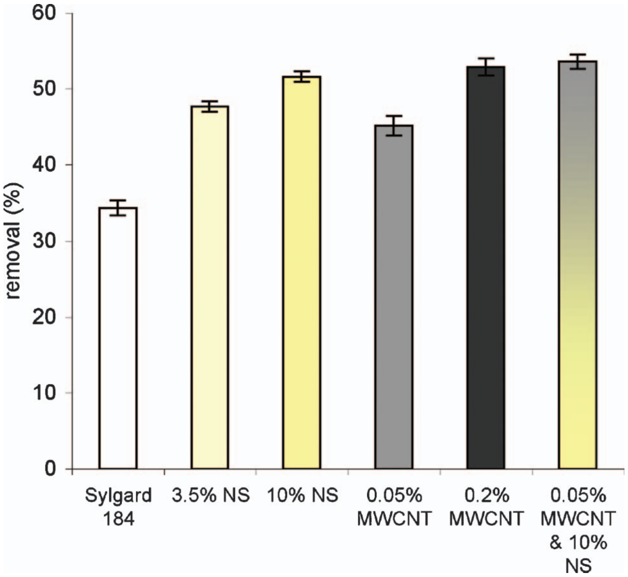

Figure 8. Percentage removal of sporelings from unfilled (Sylgard) and nanofilled silicones following exposure to a wall shear stress of 52 Pa. Each point represents the mean of 5 or 6 replicates, calculated from 216 paired readings (before and after exposure to flow) per replicate. Bars show 2 × SEM calculated from arcsine-transformed data.

Barnacle cyprid settlement assay

There was no significant difference in the settlement rate (Figure 9) on any of the filled PDMS coatings and the unfilled control (Kruskall Wallis $p = 0.35$).

Adhesion strength of adult barnacles

An ANOVA revealed that there were significant differences in the critical removal stress of barnacles with respect to coating type ($p = 0.001$). Figure 10 presents the results of a *post hoc* comparison (Dunn's test) of the treatment means. Adding NS to the PDMS increased the critical removal stress for barnacles significantly ($p < 0.05$). The addition of MWCNTs to PDMS, on the other hand, significantly ($p < 0.05$) improved the release characteristics of the elastomer. The 0.05% concentration did not, however, significantly outperform the higher, 0.2%, concentration ($p > 0.05$). Adding 0.05% MWCNTs to the 10% NS coating approximately halved the critical removal stress to the point where it was statistically indistinguishable from that of the unfilled PDMS control.

Discussion

It is well known that the fine dispersion of nanofillers in a polymer matrix and/or the strong interactions between nanoparticles and polymer chains can be responsible for mechanical reinforcement (Alexandre

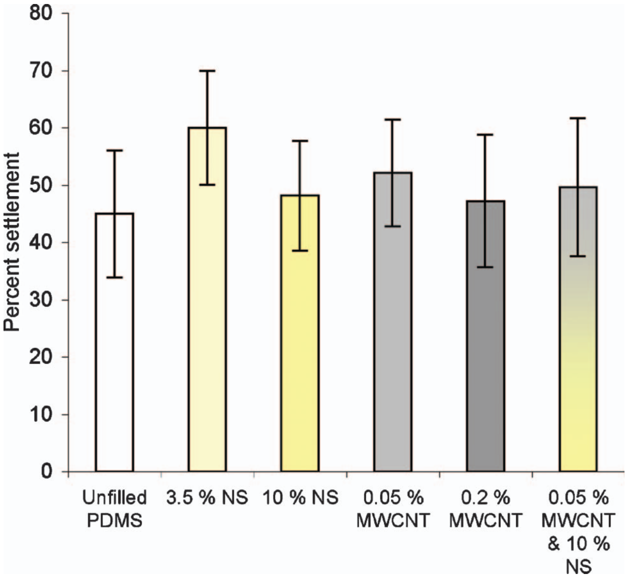

Figure 9. Percentage settlement of *B. amphitrite* cyprids on unfilled (Sylgard 184) and nanofilled PDMS after a 24-h exposure. Each bar is the mean of 12 replicates; bars show 2 × SEM.

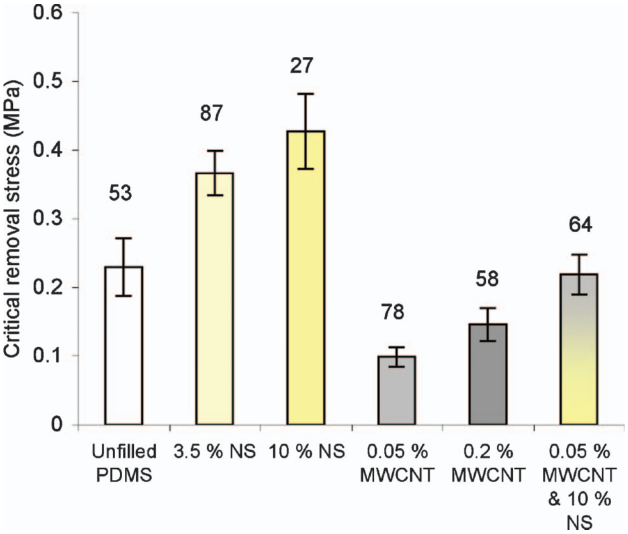

Figure 10. Critical removal stress (MPa) of ~ 0.5-cm diameter barnacles from unfilled (Sylgard 184) and nanofilled PDMS determined using an automated instrument. Each bar is the mean (sample size above); bars show 2 × SEM. The number above each bar is the number of barnacles that were used in the analysis for each formulation. The number of barnacles rejected for each surface due to >10% basal plate failure was: unfilled PDMS = 2; 3.5% NS = 9; 10% NS = 63; 0.05% MWCNT = 0; 0.2% MWCNT = 12; 0.05% MWCT and 10% NS = 15.

and Dubois 2000). A fine dispersion of the fillers within the polymer matrix is essential since aggregation of nanoparticles induces defects and causes a deterioration of the properties of the composite. The structure, the surface characteristics of the nanofillers and the nature of the interactions between both components are fundamental for the improvement of the mechanical properties. This is particularly true in the case of elastomers as demonstrated by Bokobza (2004), who reports an improvement in the mechanical properties of the PDMS matrix with the addition of natural sepiolite. Polymer–nanoparticle interactions have been shown by infrared spectroscopy, which allowed the identification of hydrogen bonds between the silanol groups on the NS surface and the siloxane backbone of the polymer (Bokobza 2004). Furthermore, a decrease of degree of equilibrium swelling in heptane was reported at higher NS loadings. This behaviour is frequently ascribed to good adhesion existing between (nano)particles and polymer chains. In the case of the MWCNT-based composites, no interference of the filler with the PDMS network was shown based on the swelling measurements and mechanical data, at least within the low filler range investigated in this study. Indeed, it is believed that the low content of MWCNTs is not sufficient to affect the mechanical properties of the composites. Thus, the bulk properties of the silicone materials proved independent of the addition of MWCNTs.

PDMS comprises a long and very flexible inorganic chain due to the long silicon–oxygen bonds and rather flat bond angles of the backbone. The rotation of methyl groups around the backbone is thus possible; the polymer chains present the methyl groups to the air interface and, adopting this molecular conformation, minimises the surface energy (Khorazani et al. 2005). The restructuring of a PDMS surface in water was demonstrated by Chen et al. (2004) using sum frequency generation (SFG) vibrational spectroscopy. The authors showed that when PDMS contacts water, methyl groups on the surface tilt more towards the surface. Recently, Beigbeder et al. (2008) have investigated the affinity between MWCNTs and silicone resin. This work demonstrates that reinforcing silicone with a very small amount of MWCNTS is one of the most efficient approaches to impart novel properties into the silicone matrix due to extremely favourable CH-pi electronic interactions involving methyl groups of the PDMS and aromatic rings of the MWCNTs. The hypothesis is that when an unfilled silicone-based coating is immersed in water, some reversible molecular reorganisation occurs which decreases unfavourable water/PDMS methyl group interactions to the benefit of water/siloxane ones. However, due to the good affinity between PDMS chains and nanofillers (MWCNTs or NS) the polymer chains become less mobile and the top surface reorganisation is no longer observed (or at least it is very reduced) when nanofillers are dispersed in silicone-based coatings. The global surface is more hydrophobic as evidenced by contact angle measurements. The surface reorganisation of (nanofilled) silicone-based coating when immersed in water is beyond the scope of this paper and will be discussed in more detail in a forthcoming publication.

Considering the data on the consequences for biological performance of incorporating different nanofillers into the coating, a range of effects was observed, some of which can be explained by current knowledge of the influence of interfacial and bulk properties on settlement and adhesion. The settlement of *Ulva* zoospores is influenced by a range of surface properties including hydrophobicity and topography (eg Callow et al. 2000, Carman et al. 2006, Schumacher et al. 2007a,b). Since reduced wettability generally stimulates settlement, the increased settlement of spores on the NS-filled coating may be a consequence of the increased hydrophobicity that results from the inclusion of this nanofiller. On the other hand, similar changes in hydrophobicity observed for MWCNT-filled coatings had a much smaller effect on spore settlement, suggesting that other factors are involved. At this stage topographic effects cannot be excluded without further work.

The settlement of barnacle cyprids is also affected by surface hydrophobicity, but the effects are species-dependent (Rittschof and Costlow 1989; O'Connor and Richardson 1994, Dahlström et al. 2004). Likewise, cyprids generally have a predilection for rough over smooth surfaces (Crisp 1974), though certain micro-textures have been shown to be inhibitory (eg Crisp and Barnes 1954, Lemire and Bourget 1996, Berntsson et al. 2000, 2004, Schumacher et al. 2007b). Nevertheless, differences in surface properties of the coatings tested here did not affect settlement of *B. amphitrite* cyprids significantly. *B. amphitrite* settlement should tend to decrease with increasing hydrophobicity of the filled surfaces, while increased topography generally has the opposite effect, though nanotopography has not previously been investigated. Evidently, the surfaces were either not sufficiently different or the effects of these stimuli cancelled each other out.

Considering now the influence of nanofillers on the adhesion strength of attached organisms, barnacle adhesion strength has been modelled using solid cylinders (so-called 'pseudobarnacles') and is proportional to $(\gamma E)^{1/2}$ where γ is the surface energy and E the modulus (Brady and Singer 2000, Kim et al. 2007). Barnacles, however, bear little resemblance to a solid cylinder and in the few studies that have examined the adhesion strength of live animals grown *in situ*, departures from pseudobarnacle adhesion mechanics have been noted (Singer et al. 2000; Sun et al. 2004; Wendt et al. 2006). Important considerations in this regard include differences in flexural rigidity of calcified barnacle bases and pseudobarnacles (Ramsay et al. 2008), and differences in the moduli of commercial and natural adhesives (Sun et al. 2004). If the addition of nanofillers to an elastomeric coating were to affect modulus, current knowledge is, therefore, insufficient for live barnacles to predict how this factor would affect adhesion strength. For more compliant, soft-fouling organisms like *Ulva*, modulus is relatively unimportant (at least within the range of modulus values encountered in practical coatings) and surface energy properties are more likely to predominate (Chaudhury et al. 2005). Because the effect of MWCNTs on coating modulus reported in this article appear to be minor, it is therefore unlikely that the improved fouling-release properties of siloxanes incorporating this nanofiller can be ascribed to effects on modulus.

The most dramatic results of this study were the reductions in critical removal stress of adult barnacles obtained by adding small amounts of MWCNTs to the unfilled PDMS and the 10% NS coating. The addition of only 0.05% MWCNTs to unfilled PDMS more than halved the critical removal stress; a higher concentration of 0.2% was less effective, possibly due to poorer dispersion of the MWCNTs. Likewise, the addition of 0.05% MWCNTs to 10% NS coating led to an ~50% reduction in removal stress. It should be noted that the results of some of these comparisons would differ substantially if the barnacles with failed bases were included in the analyses (numbers omitted are shown in the legend to Figure 10), as such failure likely accords with higher adhesion strength. Thus the coating filled with 0.05% MWCNTs performed even better than depicted in Figure 10, since all barnacles were removed cleanly from this surface. In contrast, the mean critical removal stress for the 10% NS-filled coating would have been higher, as 70% of the barnacles were removed from the analysis. Improvements in release characteristics did not reflect differences in tensile modulus or wettability and therefore other effects that the nanofillers may have that are relevant to barnacle release must be looked for. At this stage it is only possible to speculate what these may be. In the case of MWCNTs, earlier in this discussion reference was made to the influence that the strong affinity between the nanofillers and the PDMS chains may have on surface reorganisation of the coating underwater. It is well known for a variety of cell types that substratum roughness at the nanoscale influences cell adhesion (eg Curtis et al. 2001). One hypothesis, therefore, is that changes in surface rugosity could influence barnacle adhesion through changes in the secretion of barnacle cement or the bonding between the cement and the coating. Zhao and Deng (2005) reported that CNTs reduced the frictional coefficient of Ni-P coatings deposited by electroless plating. Because surface lubricity has also been implicated in fouling-release performance (Newby and Chaudhury 1997), another possibility is that the MWCNTs in PDMS may improve surface lubricity, thus favouring release. This and other hypotheses will be explored in future work.

Conclusions

It was shown that the presence of a small amount (0.05%) of MWCNTs within a silicone elastomer results in a significant enhancement of the FR properties. At the same time, the bulk mechanical properties of the coatings appear unchanged, in contrast to the surface properties. After water exposure, surface wettability was modified when fillers were present. Thus all the data indicate that independently of the bulk properties, the surface properties affect settlement, and more particularly, the FR behaviour of the filled MWCNT-based materials. In the case of NS, the higher loading (up to 10 wt%) appears to be responsible for a substantial increase in the coating stiffness as well as some tuning of the surface energy properties as shown by contact angle measurements. A future publication will report the effect of the processing/blending tool and the extent of nanofiller dispersion within the silicone matrix. A further increase in the AF performance and an improvement in the FR properties are being investigated in relation to the quality of filler dispersion throughout the polymer matrix.

Acknowledgements

The work was funded by the EC Framework 6 Integrated Project 'AMBIO' (Advanced Nanostructured Surfaces for the Control of Biofouling). This article reflects only the authors' views and the European Commission is not liable for any use that may be made of information contained therein. The authors also thank Nanocyl SA (Sambreville, Belgium) for kindly supplying the carbon nanotubes. SMPC is grateful to the Région Wallonne and the European Union (FEDER, FSE) for financial support through the Phasing-Out of Objectif-1 Hainaut: Materia Nova. SMPC thanks the "Belgian Federal Government Office Policy of Science (SSTC)" for general support in the frame of the PAI-6/27. Ms Christine Beveridge is thanked for technical assistance with the algal assays.

References

Alexandre M, Dubois P. 2000. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng. R28:1–63.

Beigbeder A, Linares M, Devalkenaere M, Degée P, Claes M, Beljonne D, Lazzaroni R, Dubois P. 2008. CH-pi interactions as the driving force for silicone-based nanocomposites with exceptional properties. Adv Mater. 20:1003–1007.

Berglin M, Lönn N, Gatenholm P. 2003. Coating modulus and barnacle bioadhesion. Biofouling. 19(Suppl):63–69.

Berntsson KM, Jonsson PR, Lejhall M, Gatenholm P. 2000. Analysis of behavioural rejection of micro-textured surfaces and implications for recruitment by the barnacle *Balanus improvisus*. J Exp Mar Biol Ecol. 251:59–83.

Berntsson KM, Jonsson PR, Larsson AI, Holdt S. 2004. Rejection of unsuitable substrata as a potential driver of aggregated settlement in the barnacle *Balanus improvisus*. Mar Ecol Prog Ser. 275:199–210.

Beyer G. 2002. Nanocomposites: a new class of flame retardants for polymers. Plast Addit Compd. 4:22–28.

Bokobza L. 2004. Elastomeric composites. I. Silicone composites. J Appl Polym Sci. 93:2095–2104.

Bokobza L, Kolodziej M. 2006. On the use of carbon nanotubes as reinforcing fillers for elastomeric materials. Polym Int. 55:1090–1098.

Bultman JD, Griffith JR. 1994. Fluoropolymer and silicone fouling-release coatings. In: Thompson MF, Nagabhushanam R, Sarojini R, Fingerman M, editors. Recent developments in biofouling control. Rotterdam: A.A. Balkema. p. 383.

Brady RF, Singer IL. 2000. Mechanical factors favoring release from fouling release coatings. Biofouling. 15:73–81.

Callow JA, Callow ME. 2006. The *Ulva* spore adhesive system. In: Smith AM, Callow JA, editors. Biological adhesives. Springer-Verlag, Berlin, Heidelberg. p. 63–78.

Callow ME, Callow JA, Pickett-Heaps JD, Wetherbee R. 1997. Primary adhesion of *Enteromorpha* (Chlorophyta, Ulvales) propagules: quantitative settlement studies and video microscopy. J Phycol. 33:938–947.

Callow ME, Callow JA, Ista LK, Coleman SE, Nolasco AC, Lopez GP. 2000. Use of self-assembled monolayers of different wettabilities to study surface selection and primary adhesion processes of green algal (*Enteromorpha*) zoospores. Appl Environ Microbiol. 66:3249–3254.

Callow ME, Jennings AR, Brennan AB, Seegert CE, Gibson A, Wilson L, Feinberg A, Baney R, Callow JA. 2002. Microtopographic cues for settlement of zoospores of the green fouling alga *Enteromorpha*. Biofouling. 18:237–245.

Carman ML, Estes TG, Feinberg AW, Schumacher JF, Wilkerson W, Wilson LH, Callow ME, Callow JA, Brennan AB. 2006. Engineered antifouling microtopographies—correlating wettability with cell attachment. Biofouling. 22:11–21.

Cassé F, Ribeiro E, Ekin A, Webster DC, Callow JA, Callow ME. 2007a. Laboratory screening of coating libraries for algal adhesion. Biofouling. 23:267–276.

Cassé F, Stafslien SJ, Bahr JA, Daniels J, Finlay JA, Callow JA, Callow ME. 2007b. Combinatorial materials research applied to the development of new surface coatings. V. Application of a spinning water-jet for the semi-high throughput assessment of the attachment strength of marine fouling algae. Biofouling. 23:121–130.

Chaudhury MK, Finlay JA, Chung JY, Callow ME, Callow JA. 2005. The influence of elastic modulus and thickness on the soft fouling alga *Ulva linza* (*Enteromorpha linza*) from polydimethyl siloxane (PDMS) ideal networks. Biofouling. 21:41–48.

Chaterjee S, Goyal A, Shah SI. 2006. Inorganic nanocomposites for the next generation photovoltaics. Matter Lett. 60:3541–3543.

Chen C, Wang J, Chen Z. 2004. Surface restructuring behavior of various types of poly(dimethylsiloxane) in water detected by SFG. Langmuir. 20:10186–10193.

Chen H, Zheng M, Sun H, Jia Q. 2007. Characterization and properties of sepiolite/polyurethane nanocomposites. Mater Sci Eng A. 445:725–730.

Clare AS. 1996. Marine natural product antifoulants: status and potential. Biofouling. 9:211–229.

Clare AS, Matsumura K. 2000. Nature and perception of barnacle settlement pheromones. Biofouling. 15:57–71.

Clare AS, Høeg JT. (2008). *Balanus amphitrite* or *Amphibalanus amphitrite*? A note on barnacle nomenclature. Biofouling. 24:55–57.

Crisp DJ. 1974. Factors influencing the settlement of marine invertebrate larvae. In: Grant PT, Mackie AM, editors. Chemoreception in marine organisms. London: Academic Press. p. 177–265.

Crisp DJ, Barnes H. 1954. The orientation and distribution of barnacles at settlement with particular reference to surface contour. J Anim Ecol. 23:143–162.

Curtis ASG, Casey B, Gallagher JO, Pasqui D, Wood MA, Wilkinson CDW. 2001. Substratum topography and the adhesion of biological cells. Are symmetry or regularity of nanotopography important? Biophys Chem. 94:275–283.

Dahlström Jonsson H, Jonsson PR, Elwing H. 2004. Suface wettability as a determinant in the settlement of the barnacle *Balanus improvisus* (Darwin). J Exp Mar Biol Ecol. 305:223–232.

de Paiva LB, Morales AR, Guimaroes TR. 2007. Structural and optical properties of polypropylene-montmorillonite nanocomposites. Mater Sci Eng A. 447:261–265.

Erva S, Bahar I, Erman B. 1998. Swelling of sodium chloride filled polybutadiene networks in water, water/acetone and water/THF mixtures. Polymer. 39:2035–2041.

Finlay JA, Fletcher BR, Callow ME, Callow JA. 2008. Effect of background colour on growth and adhesion strength of *Ulva* sporelings. Biofouling. 24:219–225.

Fusetani N. 2004. Natural products and antifouling. Nat Prod Rep. 21:94–104.

Genzer J, Efimenko K. 2006. Review: recent developments in superhydrophobic surfaces and their relevance to marine fouling. Biofouling. 22:339–360.

Hellio C, Marechal JP, Veron B, Bremer G, Clare AS, Le Gal Y. 2004. Seasonal variation of antifouling activities of marine algae from the Brittany coast (France). Mar Biotechnol. 6:67–82.

Hellio C, Tsoukatou M, Marechal JP, Aldred N, Beaupoil C, Clare AS, Vagias C, Roussis V. 2005. Inhibitory effects of Meditteranean sponge extracts and metabolites on larval settlement of the barnacle *Balanus amphitrite*. Mar Biotechnol. 7:297–305.

Iijima S. 1991. Helical microtubules of graphitic carbon. Nature. 354:56–58.

Jeffrey SW, Humphrey GF. 1975. New spectrophotometric equations for determining chlorophylls *a, b, c1* and *c2* in higher plants, algae and natural phytoplankton. Biochem Physiol Pflanz. 167:191–194.

Jelic-Mrcelic G, Sliskovic M, Antolic B. 2006. Biofouling communities on test panels coated with TBT and TBT-free copper-based antifouling paints. Biofouling. 22:293–302.

Jin MH, Feng XJ, Xi JM, Ehai J, Cho KW, Feng L. 2005. Super-hydrophobic PDMS surfaces with ultra-low adhesive force. Macromol Rapid Commun. 26:1805–1809.

Kavanagh CJ, Quinn RD, Swain GW. 2005. Observations of barnacle detachment from silicones using high-speed video. J Adhesion. 81:843–868.

Khorazani MT, Mirzadeh H, Kermani Z. 2005. Wettability of porous polydimethylsiloxane surface: morphology study. Appl Surf Sci. 242:339–345.

Kim J, Chisholm BJ, Bahr J. 2007. Adhesion study of silicone coatings: the interaction of thickness, modulus, and shear rate on adhesion force. Biofouling. 23:113–120.

Lemire M, Bourget E. 1996. Substratum heterogeneity and complexity influence micro-habitat selection of *Balanus* sp. and *Tubulariacrocea* larvae. Mar Ecol Prog Ser. 135:77–87.

Ma J, Bilotti E, Peijs T, Darr JA. 2007. Preparation of polypropylene/sepiolite nanocomposites using supercritical CO_2 assisted mixing. Eur Pol J. 43:4931–4939.

Marmur A. 2006. Superhydrophobicity fundamentals: implications for biofouling prevention. Biofouling. 22:107–115.

Newby BM, Chaudhury MK. 1997. Effect of interfacial slippage on viscoelastic adhesion. Langmuir. 13:1805–1809.

O'Connor NJ, Richardson DL. 1994. Comparative attachment of barnacle cyprids (*Balanus amphitrite* Darwin, 1854; *B. improvisus* Darwin, 1854; and *B. eburneus* Gould, 1841) to polystyrene and glass substrata. J Exp Mar Biol Ecol. 183:213–225.

Olsen SM, Pedersen LT, Laursen MH, Kiil S, Dam-Johansen K. 2007. Enzyme-based antifouling coatings: a review. Biofouling. 23:369–383.

Patwardhan SV, Taori VP, Hassan M, Agashe NR, Franklin JE, Beaucage G, Mark JE, Clarson SJ. 2006. An investigation of the properties of poly (dimethylsiloxane)-bioinspired silica hybrids. Eur Pol J. 42:167–178.

Phang Y, Aldred N, Clare AS, Callow JA, Vansco GJ. 2006. An *in situ* study of the nanomechanical properties of barnacle (*Balanus amphitrite*) cyprid cement using atomic force microscopy (AFM). Biofouling. 22: 245–250.

Ramsay DB, Dickinson GH, Orihuela B, Rittschof D, Wahl KJ. 2008. Base plate mechanics of the barnacle *Balanus amphitrite* (=*Amphibalanus amphitrite*). Biofouling. 24:109–118.

Rittschof D, Costlow JD. 1989. Bryozoan and barnacle settlement in relation to initial surface wettability: a comparison of laboratory and field studies. Scientia Mar. 53:411–416.

Schmidt D, Shah D, Giannelis EP. 2000. New advances in polymer/layered silicates nanocomposites. Curr Opin Solid State Mater Sci. 6:205–212.

Schmidt DL, Brady RF, Lam K, Schmidt DC, Chaudhury MK. 2004. Contact angle hysteresis, adhesion and marine biofouling. Langmuir. 20:2830–2836.

Schultz MP. 2007. Effects of coating roughness and biofouling on ship resistance and powering. Biofouling. 23:331–341.

Schultz MP, Finlay JA, Callow ME, Callow JA. 2000. A turbulent channel flow apparatus for the determination of the adhesion strength of microfouling organisms. Biofouling. 15:243–251.

Schultz MP, Finlay JA, Callow ME, Callow JA. 2003. Three models to relate detachment of low form fouling at laboratory and ship scale. Biofouling. 19(Suppl): 17–26.

Schumacher JF, Aldred N, Callow ME, Finlay JA, Callow JA, Clare AS, Brennan AB. 2007a. Species-specific engineered antifouling topographies: correlations between the settlement of algal zoospores and barnacle cyprids. Biofouling. 23:307–317.

Schumacher JF, Carman ML, Estes TG, Feinberg AW, Wilson LH, Callow ME, Callow JA, Finlay JA, Brennan AB. 2007b. Engineered antifouling microtopographies—effect of feature size, geometry, and roughness on settlement of zoospores of the green alga *Ulva*. Biofouling. 23:55–62.

Singer IL, Kohl JG, Patterson M. 2000. Mechanical aspects of silicone coatings for hard foulant control. Biofouling. 16:301–309.

Stein J, Truby K, Darkangelo-Wood C, Takemori M, Vallance M, Swain G, Kavanagh C, Kovach B, Schultz M, Wiebe D, et al. 2003. Structure–property relationships of silicone biofouling-release coatings: effect of silicone network architecture on pseudobarnacle attachment strengths. Biofouling. 19:87–94.

Sun MH, Luo CX, Xu LP, Ji H, Qi OY, Yu DP. 2005. Artificial lotus leaf by nanocasting. Langmuir. 21:5549–5554.

Swain GE. 1999. Redefining antifouling coatings. Paint Coat Eur. July 1999:18–25.

Tai NH, Yeh MK, Liu JH. 2004. Enhancement of the mechanical properties of carbon nanotube/phenolic composites using a carbon nanotube network as the reinforcement. Carbon. 42:2774–2777.

Townsin RL. 2003. The ship hull fouling penalty. Biofouling. 19(Suppl):9–15.

Wendt DE, Kowalke GL, Kim J, Singer IL. 2006. Factors that influence coatings performance: the effect of coating thickness on basal plate morphology, growth and critical removal stress of the barnacle *Balanus amphitrite*. Biofouling. 22:1–9.

Yaobang Z, Wencheng F, Lu W, Xiaobo L. 2004. Processing and property of MWNT/HDPE composite. Carbon. 42:271–277.

Zhang ZH, Muller R, Froelich D. 1989. Determination of crosslinking density of polymer networks by mechanical data in simple extension and by swelling degree at equilibrium. Polymer. 30:2060–2062.

Zhao G, Deng F. 2005. Electroless plating of Ni-P-CNTs composite coating. Key Eng Mater. 280–283: 1445–1448.