

Preventing algae adhesion using lubricant-modified polydimethylsiloxane/polythiourethane nanocomposite



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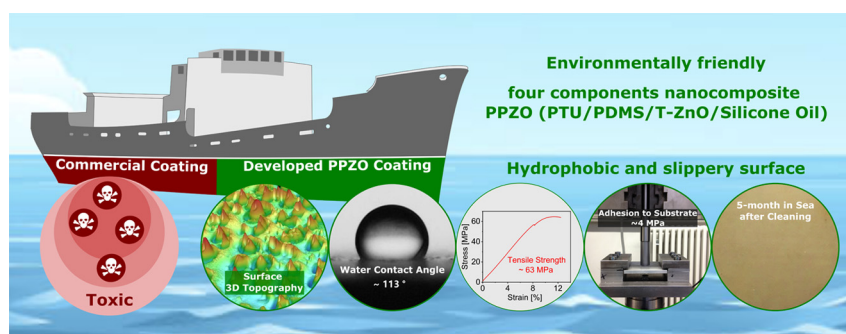
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HIGHLIGHTS

- An environmentally friendly nanocomposite for marine biofouling control was developed.
- The nanocomposite consists of four components (polythiourethane, polydimethylsiloxane, tetrapodal-shaped ZnO microparticles, and silicone oil).
- The nanocomposite has high tensile strength and good adhesion to substrates.
- The permanent attachment of algae was prevented by the incorporation of silicone oil.

GRAPHICAL ABSTRACT



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ABSTRACT

To meet the need for an environmentally friendly fouling-release coating with high mechanical strength and good adhesion to substrates, a four-component nanocomposite was developed by a simple and industrially applicable blending approach. The nanocomposite consists of mechanically stable matrix polythiourethane (PTU), 1 wt% low surface free energy and rubber-like polydimethylsiloxane (PDMS), 1 wt% lubricant silicone oil, and 1 wt% tetrapodal shaped micro-nano ZnO (t-ZnO) filler particles, hereafter named PPZO. The rubber-like PDMS formed microdomains at the PTU/air interface, while silicone oil was distributed between the PDMS microdomains. The tensile strength of PPZO nanocomposite was approximately 63 MPa, two to four hundred times higher than the tensile strength of previously reported oil-modified coatings. The adhesion strength of PPZO to the substrate was 30 times higher than that of pure PDMS. After a five-month dynamic field test, the PPZO surface revealed much less biofouling than the references (AlMg3 and PTU), confirming its long-term biofouling control property. The attached algae on PPZO could easily and completely be removed by gentle brush cleaning. The good biofouling control property of PPZO can be attributed to the increased water repellency (signified by the increased water contact angle) and the surface slippage by silicone oil incorporation.

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1. Introduction

Marine biofouling is the accumulation and growth of micro- and macroorganisms, like aquatic plants and animals, on surfaces immersed in seawater [1]. Formation of marine biofouling usually occurs in four stages: conditioning with molecules such as proteins

and carbohydrates, soft microfouler settlement and biofilm formation (e.g., composed of bacteria and diatoms), soft macrofouler settlement (e.g., algae), and hard fouler settlement (e.g., barnacles and mussels) [2]. Although this model of biofouling formation is generally accepted, it suffers from an oversimplification. Many organisms (e.g., motile zoospores of the algae *Ulva linza*) can attach to the pristine surfaces even before the microfilm formation [2,3]. Especially in commercial shipping, marine biofouling causes serious problems, such as surface deterioration and increased roughness of a ship hull, resulting in additional fuel consumption and increased CO₂ emission [4]. Moreover, the attached organisms can be introduced into non-native environments through ship transport, leading to marine biological invasions [4].

To prevent biofouling, various antifouling coatings have been developed. Since the 1960s, tributyltin (TBT)-based self-polishing antifouling coatings have been introduced and applied to ship hulls where TBT leached out continuously to the seawater [5]. Despite being an effective biocide, TBT showed to be persistent in seawater and soil, causing a negative impact on both fouling organisms and non-fouling aquatic life [6,7]. As a result, utilizing TBT-based coatings for marine applications has been prohibited since the implementation of the International Maritime Organization Treaty on biocides in 2008 [8]. The current commercial antifouling coatings usually contain a high level of copper compounds as an alternative biocide to TBT [9,10]. Copper-containing coatings are less toxic than TBT-containing ones, but high copper levels are detected in areas of heavy boat traffic and may also cause environmental problems [11,12]. Thus, copper-containing antifouling coatings may face prohibition by environmental regulations in the near future [12].

Therefore, modern research has been focused on developing environmentally friendly alternatives to the current biocide-based antifouling coatings. For example, based on low surface free energy and nano/microroughness of the material surface, fouling-release coatings have been developed [13–15]. Thus, marine organisms can only weakly attach to the coating surface and can be easily removed when subjected to shear force, e.g., resulting from ship movement [4,16]. Due to the low surface free energy and low elastic modulus, polydimethylsiloxane (PDMS) is suitable and widely investigated for the fabrication of fouling-release coatings [17–22]. By incorporating various nanoparticles (e.g., graphene oxide anchored with alumina nanorods, β -MnO₂ nanorods, nano-magnetite, SiC nanowires, spherical silver, etc.) into the PDMS matrix, Selim et al. developed PDMS-based coatings, exhibiting good fouling-release properties [23–28]. The addition of the nanoparticles into the PDMS matrix significantly increased the hydrophobicity of the nanocomposite, leading to a superhydrophobic fouling-release surface [29–32]. However, the application of PDMS-based coatings is often limited due to their poor mechanical performance and low adhesion strength to substrates.

To overcome the drawbacks of coatings using pure PDMS as a matrix, polythiourethane (PTU)/PDMS nanocomposites reinforced with tetrapodal-shaped micro-nano ZnO particles (t-ZnO) have been fabricated. The t-ZnO is produced through a flame transport synthesis (FTS) approach [33,34]. Used as a matrix, PTU meets the requirements for marine applications, such as good mechanical and UV stability, high adhesion strength to substrates and thus abrasion resistance [35–38]. Due to phase-separation between PDMS and PTU during the polymerization process of the nanocomposite, micro-sized PDMS domains were formed at the PTU/air interface, which benefits the fouling-release performance of the nanocomposite. The incorporation of t-ZnO in the polymer matrix improves the mechanical properties and the adhesion strength to substrates of the nanocomposite. It was shown that the PTU containing 1 wt% PDMS and 1 wt% t-ZnO (PPZ) exhibited promising fouling-release properties in terms of hard macrofouling (i.e. bar-

nacles). Barnacles adhering to the PPZ surface could be easily removed without leaving any calcified residues, similar to pure PDMS, in contrast to other reference materials such as pure PTU, AlMg₃, and PVC [33,34].

PDMS-based fouling-release coatings usually have poor biofouling control performance under static conditions and require a certain shear force to release the attached organisms, e.g., by ship movement (the minimum velocity of 15 knots to release barnacles from PDMS surfaces) [13,39]. It has been shown that light microalgal slime and colonization by macroalgae can increase drag resistance by 11% and 34%, respectively [40]. Various approaches have been proposed to improve the antifouling and fouling-release properties of PDMS-based coatings, such as the incorporation of an antifouling agent, fabrication of superhydrophobic or amphiphilic surfaces by mixing micro-/nanoparticles or hydrophilic components into PDMS, and increase of the surface slippage with the addition of oily lubricants [39,41–43]. Silicone oil is widely used in industrial products and medical fields due to several unique properties: good thermal stability, non-toxicity, high lubricity, and stable film strip formations [44–46]. The incorporation of non-reactive silicone oil into PDMS-based coatings has been reported since 1977 [47]. Although there have been concerns about possible issues in terms of the silicone oil released from coatings into marine environments, no direct influence on marine organisms has been found due to a negligible amount of silicone oil released and its extremely low toxicity [48,49]. It was shown that non-bonding silicone oil provided the coating surface with high lubricity, thereby resulting in reduced adhesion of marine organisms (e.g. algae, mussels, etc.) [43,50].

Thus, to optimize the fouling-release performance and improve the algae resistance of the previously developed PPZ nanocomposite, in this study, silicone oil was incorporated to fabricate a four-component nanocomposite consisting of a mechanically stable matrix PTU, 1 wt% low surface free energy and rubber-like PDMS, 1 wt% lubricant silicone oil, and 1 wt% t-ZnO filler particles, hereafter named PPZO. Silicone oils with different functional groups and viscosity were used, and their influence on the surface wettability and mechanical properties of the nanocomposite were characterized. The incorporation of 1 wt% silicone oil (vinyl300) improved the hydrophobicity of the nanocomposite while having no negative effect on mechanical properties. The PPZO nanocomposite with 1 wt% silicone oil (vinyl300) was further investigated in terms of its surface morphology and adhesion strength to substrates. The high tensile strength and adhesion to substrates of the nanocomposite originated from the PTU matrix and were reinforced by t-ZnO. The fouling-release performance of the PPZO was evaluated in the Baltic Sea under dynamic biofouling testing. The easy-to-clean property of PPZO in terms of algae adhesion was compared with reference material variations (AlMg₃, PTU, PDMS, and PPZ). The good fouling-release and easy-to-clean performance of the nanocomposite is attributed to the formation of PDMS microdomains and the presence of silicone oil at the PTU/air interface, which increases the surface hydrophobicity and slippage.

2. Materials and methods

2.1. Materials

The solvent-free, aliphatic, tetrafunctional two-component thermoset PTU was supplied by Fluid & Prozesstechnik (Waltershausen, Germany). PTU polymerizes by the polyaddition reaction of aliphatic 1,6-diisocyanatohexane (HDI) with a density of 1.15 g/cm³ and tetrafunctional pentaerythritoltrimer (3-mercaptopropionate) (PETMP) with a density of 1.28 g/cm³. The rubber-like silicone component for the polymer blend, PDMS Elas-

tosil E43 with a density of 1.09 g/cm³, was purchased from Wacker Chemie AG (Munich, Germany). The t-ZnO particles (for details see [Supplementary Material, Fig. S1](#)) with a mean arm length of 50 μm were produced at Phi-Stone AG (Kiel, Germany). The silicone oils used in this study and their properties are listed in [Table 1](#). The AlMg3 (EN AW-5754) substrates were purchased from Doone GmbH (Bielefeld, Germany).

2.2. Sample preparation

The rubber-like PDMS, silicone oil, and t-ZnO were added and dispersed in the PETMP component of the PTU by using a laboratory disperser (Netzsch MiniMaster Disperser (Netzsch-Feinmahltechnik GmbH, Selb, Germany) at a rotation speed of 6000 rpm for 15 min. Subsequently, the HDI component was added to the pre-mixture and stirred in by hand for 1 min. The mixing ratio of the two components HDI to PETMP in the nanocomposite was kept 1:1.4 by weight. The rubber-like PDMS, silicone oil, and t-ZnO were all added at 1 wt% of the final polymer mixture. The experiment parameters for dispersion were selected based on previous studies [33,34]. The prepared mixture was either cast into silicone molds or applied on AlMg3 substrates by paint brushing for further characterization. All samples were cured at 85 °C for 24 h in an atmospheric furnace (Heraeus Instruments, Hanau, Germany).

2.3. Surface characterization

To evaluate the wetting properties of the polymer blend, water contact angle measurements were performed with a custom-made contact angle measuring setup (Faculty of Engineering, Kiel University, Kiel, Germany) by the sessile drop method with a distilled water drop volume of 3 μL. The measurements of five droplets were conducted for each sample surface, the mean values and the corresponding standard deviations were calculated for all material variations.

To obtain information on the chemical composition of the nanocomposite surface, Raman spectroscopy was performed with a confocal Raman spectrometer (Witec Alpha 300RA, Ulm, Germany), incorporating an Ar laser of 532 nm wavelength. To evaluate the presence of each component at the PTU/air and PTU/substrate interfaces, measurements were performed on top and backside of the cured polymer blend.

The 3D-laser scanning confocal microscope VK-X (Keyence Corporation, Osaka, Japan) was used to investigate surface topography and roughness at a magnification of 25x and 100x. The measurement light source was a red semiconductor laser with a wavelength of 658 nm.

2.4. Mechanical testing

The dog-bone-shaped tensile test specimens (20 mm × 5 mm × 1 mm) were prepared according to DIN EN ISO 527-2 by casting the polymer mixture into the silicone molds.

Table 1
Silicone oils investigated in this study.

Silicone oils (Abbreviation)	Functional group	Viscosity (cSt)	Company
Vinyl300	Vinyl	300	abcr GmbH (Karlsruhe, Germany)
Vinyl3500		3500	
Hydroxyl25	Hydroxyl	25	Sigma-Aldrich Chemie GmbH (Taufkirchen bei München, Germany)
Hydroxyl2550		2550–	
		3570	
Phenyl1000	Phenyl	1000	

To investigate the influence of silicone oil on the mechanical properties of the polymer nanocomposites, tensile tests were performed with a Zwick 1445 universal tensile testing machine (Zwick GmbH und Co. KG, Ulm, Germany). An initial load of 5 N and a constant strain rate of 5 mm/min were used for all measurements. Eight specimens were measured for each material variation. The mean values with corresponding standard deviations of the tensile strength and elongation at fracture were calculated. For statistical evaluation, a one-way analysis of variance (one-way ANOVA) followed by a Tukey test (significance level of 0.05) was performed by OriginLab (OriginLab Corporation, Northampton, MA, USA).

2.5. Adhesion to substrate

To evaluate the adhesion strength, the pull-off test of the coating from the AlMg3 substrates was conducted. The tests were based on DIN EN ISO 4624, which is commonly used for investigating lacquer systems on metal substrates. Rectangular 80 mm*80 mm AlMg3 plates with a thickness of 6 mm were used as substrates which were coated with different material variations (except for pure PDMS). Cylindrical AlMg3 stamps with a diameter of 20 mm were glued to the center of the prepared surfaces by cyanoacrylate glue (Henkel AG & Co. KGaA, Düsseldorf, Germany) and dried at room temperature for two days (for details see [Supplementary Material, Fig. S2](#)). For testing of pure PDMS, AlMg3 cylinders were glued to AlMg3 substrates by pure PDMS. The adhesion testing was conducted with a Zwick 1445 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany). The minimum tensile stress to pull off the cylinders from the substrates was measured to calculate the adhesion strength. The adhesion test was performed with a pre-load of 10 N and a constant test speed of 1 mm/min. Five samples of each variation were prepared to calculate the mean value and standard deviation.

2.6. Peeling-off test

To evaluate the potential of the nanocomposite to be used as the fouling-release coating, the 90° peeling-off test on samples' surfaces under standardized conditions was performed. The samples were prepared by applying the polymer on AlMg3 substrates (80 mm × 25 mm × 3 mm) with painting brushes. For peeling-off tests, the adhesive tapes (Tesa classic tapes, Tesa SE, Norderstedt, Germany) with a width of 19 mm were pressed on the sample surface by covering a flat AlMg3 substrate with a normal force of 150 N. The 90° peeling-off tests were performed with the Quick Test machine (Prüfpartner GmbH, Langenfeld, Germany), according to ISO 29862:2007 at a loading speed of 360 mm/min. The average adhesive force with an effective length of 50 mm was calculated. Six measurements per material variation were performed, and the mean values with the corresponding standard deviations were calculated.

2.7. Biofouling field experiment

To evaluate the fouling-release properties of the polymer nanocomposite, dynamic biofouling immersion tests were conducted at the Baltic Sea (Strande Harbor, Germany) from June 2018 to November 2018. The nanocomposite was coated on AlMg3 substrates (100 mm × 100 mm × 3 mm) by painting brushes. AlMg3, PTU, PDMS, and PPZ were prepared as reference samples. Three samples of each variation were fixed vertically on the aluminum disc connected to a motor and switched on for 30-minute rotation every week (for details see [Supplementary Material, Fig. S3](#)) [16]. The samples can achieve a linear velocity of up to 7

knots. Biofouling level was observed and recorded by an underwater camera (Olympus TG-4, Olympus Corporation, Tokyo, Japan).

2.8. Cleaning experiment

Fouling-release properties of the material variations were investigated after five-month dynamic immersion and evaluated by brush cleaning. Therefore, an electrically operated rotating brush with a diameter of 12 mm, a rotation speed of around 1000 rpm, and an applied pressure of 20 kPa was used. The surface contact time was 5 s for each area; results were recorded by the camera (Olympus TG-4, Olympus Corporation, Tokyo, Japan).

3. Results and discussion

3.1. Selection of silicone oil

To find a suitable silicone oil for the preparation of polymer nanocomposites, the influence of different silicone oils (vinyl300, vinyl3500, hydroxyl25, hydroxyl2550, phenyl1000) on the surface wettability of the nanocomposite was investigated. Thus, 1 wt% of silicone oil was incorporated into the PPZ nanocomposite during the mixing process. The water contact angle of different silicone oil-modified PPZ nanocomposites is shown in Fig. 1.

The contact angle of PPZ with both vinyl-functionalized silicone oils (vinyl300 and vinyl3500) showed the highest contact angle ($\sim 113^\circ$) of all variations and was slightly higher than that of PPZ without silicone oil ($\sim 110^\circ$). No significant influence of the viscosity of vinyl-functionalized silicone oil on the contact angle was found. The introduction of hydroxyl- and phenyl-functionalized silicone oils on the surface led to a decrease in the contact angle of the PPZ nanocomposite.

Influence of different types of silicone oil on the contact angle can be attributed to the different polarities of functional groups within the silicone oils. The hydroxyl group is polar and hydrophilic, while the vinyl group is nonpolar and hydrophobic, resulting in different wettability of silicone oils [51,52] (for details see Supplementary Material, Table S1). Previously, it was shown that incorpo-

ration of oils that increase hydrophobicity of the PDMS surface could improve the fouling-release capability of the coating [48]. As the fouling-release property of a coating is closely related to its hydrophobicity [49,53], silicone oil should not decrease the hydrophobicity of PPZ nanocomposite. This condition was fulfilled by the incorporation of vinyl-functionalized silicone oil.

Although the incorporation of silicone oil in a coating benefits from its surface properties, it usually leads to a decrease in mechanical properties of the matrix materials [54,55]. Thus, the tensile strength of the different silicone oil-modified PPZ nanocomposites was measured. Mean values and their corresponding standard deviations are shown in Fig. 2.

For all variations except for the variation with 1 wt% vinyl300, a significant reduction of the tensile strength compared to PPZ without oil was observed. For all types of silicone oil, the tensile strength of the nanocomposite decreased with an increase in the oil viscosity.

This may be attributed to the diffusion of silicone oil into the PTU matrix during the phase separation and curing of PTU. As the molecular weight, and hence viscosity of the silicone oil increased, the diffusion of the silicone oil from the bulk of the PTU matrix to the surface became more difficult, resulting in more silicone oil being present in the bulk of the nanocomposite rather than on the nanocomposite/air interface [56]. The more severe influence of the hydroxyl-functionalized silicone oil on the tensile strength may be due to its hydrophilicity compared to vinyl- and phenyl-functionalized silicone oils. Thus, more hydroxyl-functionalized silicone oil was retained in the bulk of the hydrophilic PTU matrix, leading to a decrease in tensile strength [57].

Showing the best performance in both hydrophobicity and mechanical properties of the new nanocomposite, vinyl300 oil was selected for further evaluation. Thus, the PTU/ 1 wt% PDMS/ 1 wt% t-ZnO/ 1 wt% vinyl300 (PPZO) nanocomposite was prepared and further characterized.

3.2. Physico-chemical characterization of PPZO

To investigate the distribution of the vinyl300 silicone oil and its influence on PDMS microdomain formation, the surface of the

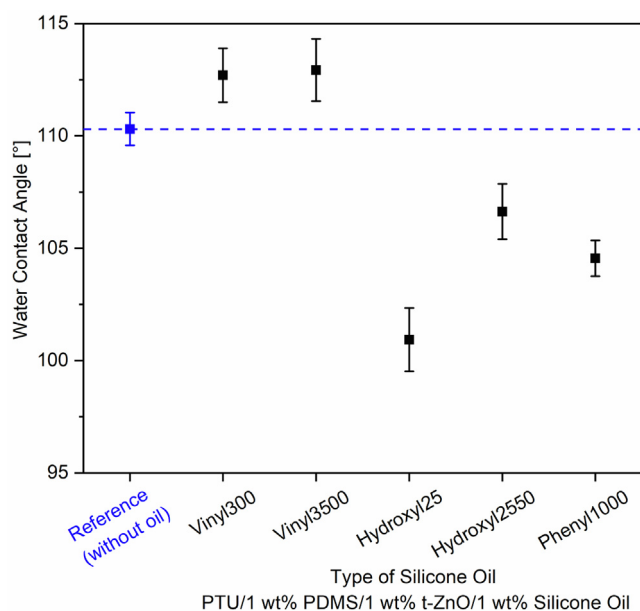


Fig. 1. Influence of 1 wt% different silicone oil addition on surface wettability of PTU/ 1 wt% PDMS/ 1 wt% t-ZnO (PPZ) nanocomposite. Mean values with the corresponding standard deviations of water contact angle are shown.

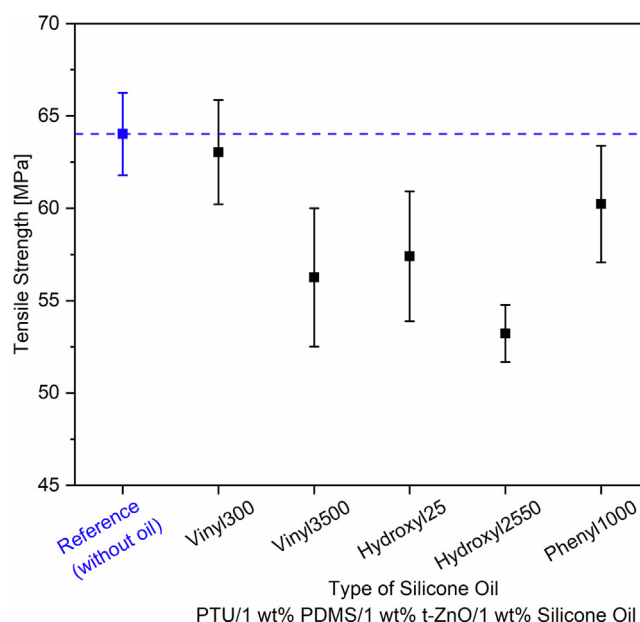


Fig. 2. Tensile strength of PTU/ 1 wt% PDMS/ 1 wt% t-ZnO nanocomposite with 1 wt% of different types of silicone oil. Mean values with the corresponding standard deviations of tensile strength are shown.

PPZO nanocomposite was characterized by a 3D-laser scanning confocal microscope (shown in Fig. 3).

Due to differences in surface free energy and density between each component, the polymer components of PPZO did not form a homogeneous mixture, but a phase-separated blend with PDMS microdomains forming at the PTU/air interface (Fig. 3). The cone-like PDMS-rubber microdomains at the PTU/air interface can clearly be distinguished from the PTU matrix, while liquid silicone oil distributed at the PTU/air interface surrounds the PDMS microdomains and forms a thin oil layer between the solid PDMS microdomains.

As the low surface free energy of PDMS was found to be the decisive factor for the presence of PDMS microdomains at the PTU/air interface [33,34], presence of silicone oil at the surface can be attributed to the same mechanism. For a real application under complex marine conditions, the surface structure and composition should be long-term stable. The stability of the PDMS microdomains at the PTU/air interface is provided by mechanical interlocking of the PDMS domains and PTU matrix, which was confirmed in the previous studies [33,34]. To retain the silicone oil stable on the surface, the fabrication process of lubricant-infused surfaces usually includes the construction of micro-/nano-sized roughness features, such as pillars [58]. On such structured surfaces, the distribution and retention of the lubricant are facilitated due to Van der Waals and capillary forces [59,60]. Capillary forces trap the oily lubricant on the structured surface since the capillary length of the lubricant (~ 1 mm under Earth's gravity) is higher than the length of the surface microstructures [61]. Therefore, the cone-like PDMS microdomains on the PPZO surface are beneficial to hold and stabilize the silicone oil. The stability of the oil on the nanocomposite surface was proven by a 5-month dynamic bio-fouling trial and is discussed in detail in Chapter 3.3.

To investigate chemical composition of the surface and the influence of the silicone oil on the curing process of the nanocomposite, Raman spectra of the nanocomposite were obtained and

compared with the spectra of the pure components (shown in Fig. 4).

The Raman spectrum of area (1) indicated and confirmed the existence of the silicone oil layer on the PPZO surface (Fig. 4a, 4b). On the backside of the coating, no silicone oil was detected by Raman spectroscopy. In contrast, a high amount of t-ZnO was detected on the backside of the coating, as shown in Fig. 4c (for details see Supplementary Material, Fig. S4), which can be explained by the higher density of ZnO compared to the PTU matrix [33]. Comparing the Raman spectra of the PTU area on PPZO with that of pure PTU, no additional molecular vibrations were found at 2272 cm^{-1} and 2545 cm^{-1} , which would arise from unreacted S-H groups from the PETMP component and unreacted -NCO groups from the HDI component, respectively. Thus, it can be assumed that silicone oil did not influence the polyaddition reaction of the PTU matrix.

The high adhesion strength of a fouling-release coating to the substrate is essential for its long-term stability in marine conditions. Therefore, a tie-coat (middle layer) is usually needed to ensure good adhesion between a fouling-release coating (topcoat) and the primer anti-corrosion coating (bottom layer) [62]. In the case of a lubricant-infused coating, the interface bonding between the coating and substrate is supposed to be weakened due to the presence of a lubricant [58]. Thus, the development of lubricant-incorporated coatings with good adhesion to the substrate is required.

To investigate the influence of adding silicone oil into the PPZ nanocomposite on the adhesion strength to AlMg3 substrates, the pull-off test was performed (shown in Fig. 5).

The adhesion strength of pure PTU was around 30 times higher than that of pure PDMS (0.12 ± 0.01 MPa). For both the PPZ and PPZO nanocomposites, the adhesion strength showed similar values as PTU, namely around 4 MPa. This result showed that the addition of silicone oil had no negative effect on the adhesion strength of the nanocomposite to the AlMg3 substrates.

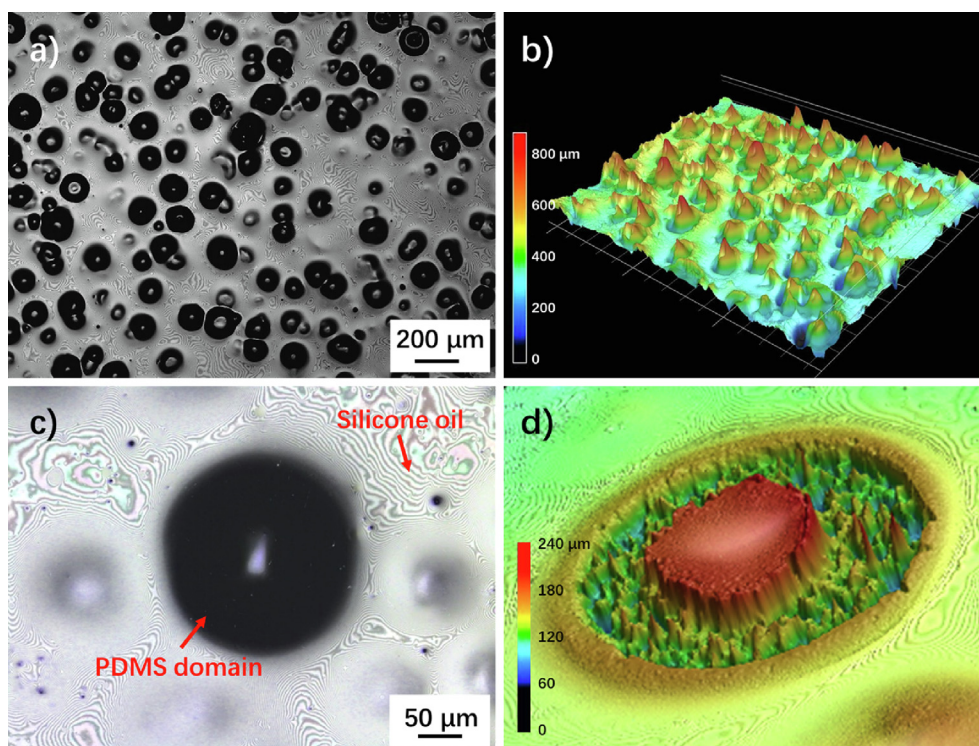


Fig. 3. 2D and 3D confocal microscopy images of the PPZO surface, showing rubber-like PDMS microdomains surrounded by the PTU matrix and silicone oil: a, b) magnification 25x; c, d) magnification 100x.

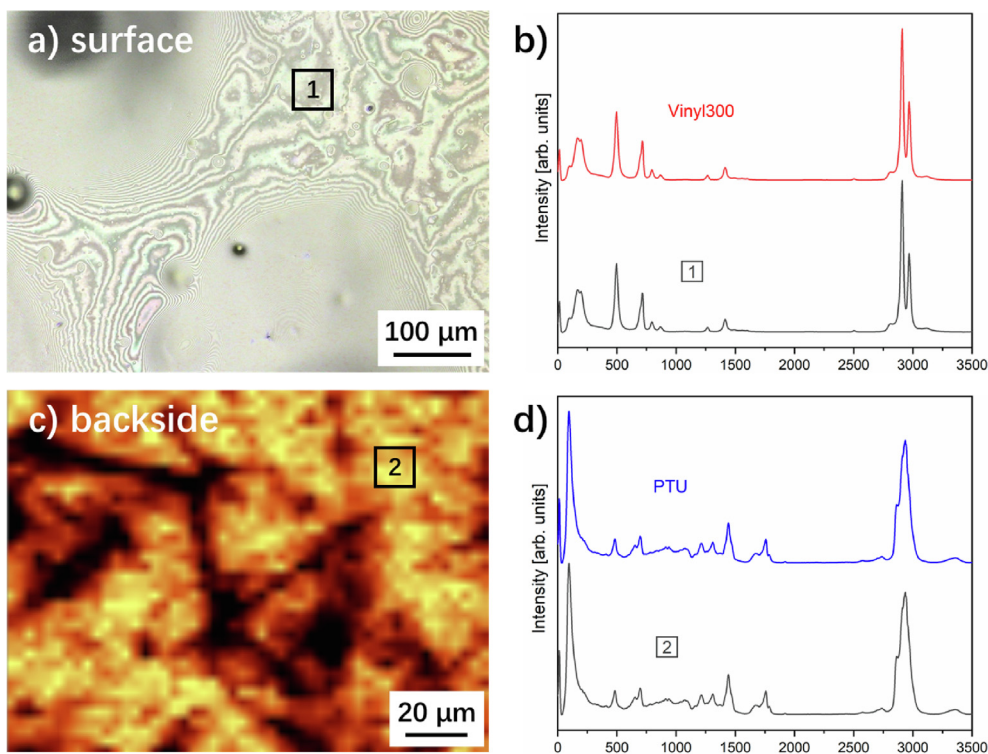


Fig. 4. Characterization of the surface and backside of the PPZO by Raman spectroscopy. a) Visualization of silicone oil on the PPZO surface (topside, i.e., the polymer/air interface), b) Raman spectra of pure vinyl300, as a reference, and the silicone oil (marked with 1) on the PPZO surface. c) Filtered Raman-images of PTU and t-ZnO on the backside of PPZO. The PTU appears in yellow with respect to the C = O bonding at 1750 cm^{-1} , whereas the t-ZnO appears in dark red. d) Raman spectra of pure PTU, as a reference, and PTU area (marked with 2) on the backside of the PPZO.

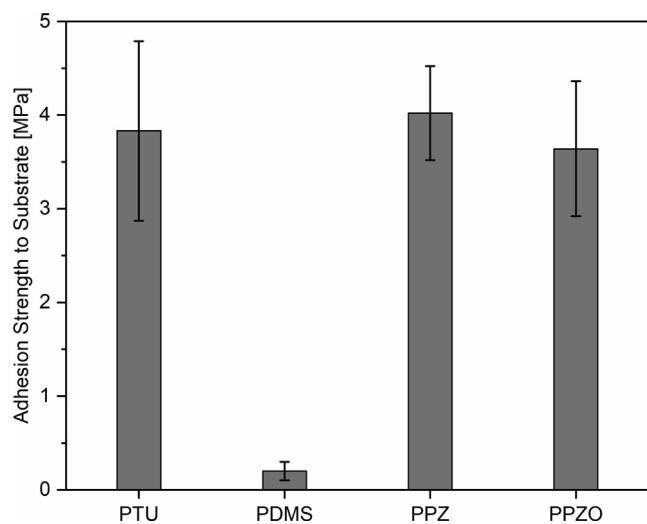


Fig. 5. Substrate adhesion strength of different polymer systems: pure PTU, pure PDMS, PPZ, and PPZO nanocomposite.

As shown from the Raman spectra (Fig. 4), the PDMS microdomains and the silicone oil were distributed mainly on the coating surface, while t-ZnO dominated on the backside of the coating. Thus, the good adhesion to substrates of PPZO was inherited from the PTU matrix and reinforced by t-ZnO particles. As shown in previous research [63], t-ZnO can be used for joining low surface energy polymers such as polytetrafluoroethylene (PTFE) and silicone by mechanical interlocking. Hölken et al. [36] previously reported the influence of t-ZnO on adhesion of PTU to AlMg3 substrates, where the adhesive strength was improved by the addition

of t-ZnO instead of spherical ZnO. Sandblasting of the AlMg3 substrates and unique particle geometry of t-ZnO resulted in mechanical interlocking between t-ZnO and the surface of the substrate.

3.3. Fouling-release and easy-to-clean properties of PPZO

The fouling-release property of the PPZO nanocomposite was characterized by peeling-off tests with adhesive tapes, while AlMg3, PTU, PDMS, and PPZ were used as reference surfaces (Fig. 6).

The peeling-off forces of the adhesive tapes from AlMg3 and PTU were around 202 N/m and 207 N/m, respectively. For the other

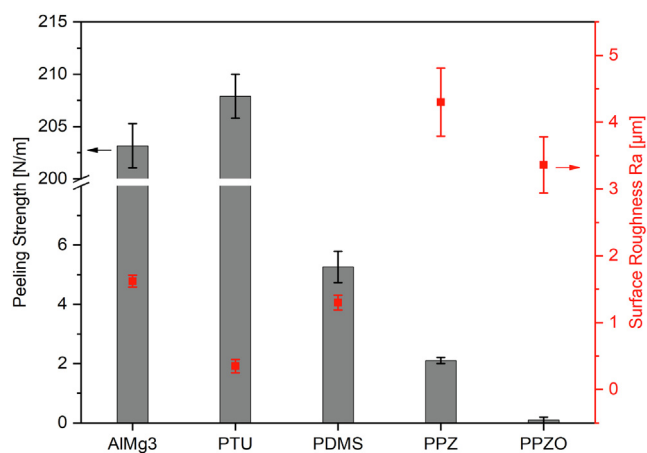


Fig. 6. Bar graph: peeling off forces of adhesive tapes from the surfaces of AlMg3, PTU, PDMS, PPZ, and PPZO. Dot graph: the surface roughness Ra of respective material variations.

variations (i.e., PDMS, PPZ, PPZO), the peeling-off force was always lower than 10 N/m.

The low peeling-off force from PDMS can be explained by the low surface free energy of PDMS [33]. As for the PPZ nanocomposite, the low peeling-off force can be attributed to the formation of PDMS microdomains on the surface, which reduced the polar part at the PTU/air interface and increased the roughness of the surface, as discussed in the previous studies [33,34]. Even though PPZO showed a smoother surface compared to PPZ, the peeling-off force was further reduced due to the oil layer on the surface.

The fouling-release performance of the nanocomposite was evaluated under dynamic biofouling testing in the Baltic Sea. The dynamic rotation was switched on for 30 mins every week. Fig. 7 shows material surfaces before and after 6 weeks of immersion in the Baltic Sea.

After six weeks of immersion in the summer season, AlMg3 and PTU surfaces showed strong fouling by long green and brown algae, which were not detached by shear forces due to rotation. PPZ nanocomposite had fewer algae attachments compared to

AlMg3 and PTU surfaces after 6 weeks of immersion. The sixth-time 30 mins rotation contributed to the partial release of the algae. There was a strong reduction of fouling organisms on PDMS and PPZO surfaces. The surfaces of PDMS and PPZO showed a similar degree of biofouling, which was mainly composed of a slime film and loosely attached brown algae. There were almost no green algae on both surfaces. After 30 mins dynamic rotation, most brown algae were released from both surfaces, even though the rotation speed was lower than 7 knots.

The presence of remaining brown algae and slime on both PDMS and PPZO can be attributed to the limited rotational speed of dynamic testing, as it was reported that the accumulated slime could not be released from ships even at high speeds (>30 knots) [13]. When comparing the surfaces of PPZ and PPZO, one can state that the incorporation of silicone oil effectively reduces algae attachment for at least 6 weeks, which can be attributed to the silicone oil layer retained and stabilized by the PDMS cone-like microdomains. This result is in accordance with a study conducted by Wilson et al., where the combination of lubricant and micropillar structures significantly reduced the number of attached spores compared to the smooth and unmodified PDMS surfaces exposed to turbulent flow in a flow channel [64].

To evaluate the easy-to-clean properties of the nanocomposite, surfaces which faced 5 months of immersion were gently cleaned with brushes. Fig. 8 shows the surfaces before and after cleaning.

Before cleaning, AlMg3 and PTU surfaces showed the highest fouling degree of green and brown algae, while fewer green algae were found on the PPZ surface. Although brush cleaning of AlMg3, PTU, and PPZ showed that most attached organisms were removed, some residues of green algae were left behind. Regarding the PDMS surface, almost no green algae were found, and the surface was well cleaned without any organism residues. Similarly, only a few algae were attached on the PPZO surface. Applying the cleaning procedure to the PPZO surface led to the complete removal of all attached organisms. The dynamic biofouling testing and the cleaning experiment illustrated the improved biofouling control performance and easy-to-clean property of PPZO in terms of algae adhesion compared to PPZ nanocomposites.

The long-term application of lubricant-infused surfaces is usually hindered by poor underwater stability of the lubricant layer [58]. Natural drainage in seawater is one potential reason to decay the oil layer, while the shear force is another potential effect to cause drainage of oil on the surface [65]. In our study, the five-month sea immersion verified the long-term biofouling control property of PPZO, which indicated the good stability of the silicone oil on the coating surface (for details see [Supplementary Material, Figs. S7 and S8](#)). As discussed above, the stability of silicone oil was attributed to the PDMS cone-like microdomains. Moreover, the silicone oil used in this study has a low viscosity (300 cSt). It was shown that a less viscous lubricant could be retained better on the surface immersed in the same external liquid [66]. Incorporation of oil with lower viscosity (50 cSt) in PDMS significantly decreased the number of spore settlements and improved the release of the attached spores compared to highly viscous oil (5000 cSt) [64].

The improved algae prevention of PPZO compared to PPZ can be attributed to the inhibition of the spore anchoring mechanisms. The green algal genus *Ulva* (syn. *Enteromorpha*) is the most common macroalga causing biofouling problems on man-made surfaces (e.g., buoys, ships, and submarines) throughout the world [67]. *Ulva* can withstand various environmental conditions and antifouling coatings [64]. Before permanent adhesion, the motile zoospores exhibit a characteristic pre-settlement behavior, including a change from random swimming to a “searching” pattern of exploration close to the surface. During the searching phase, a pad of elastic material is sometimes extruded, and if the spore con-

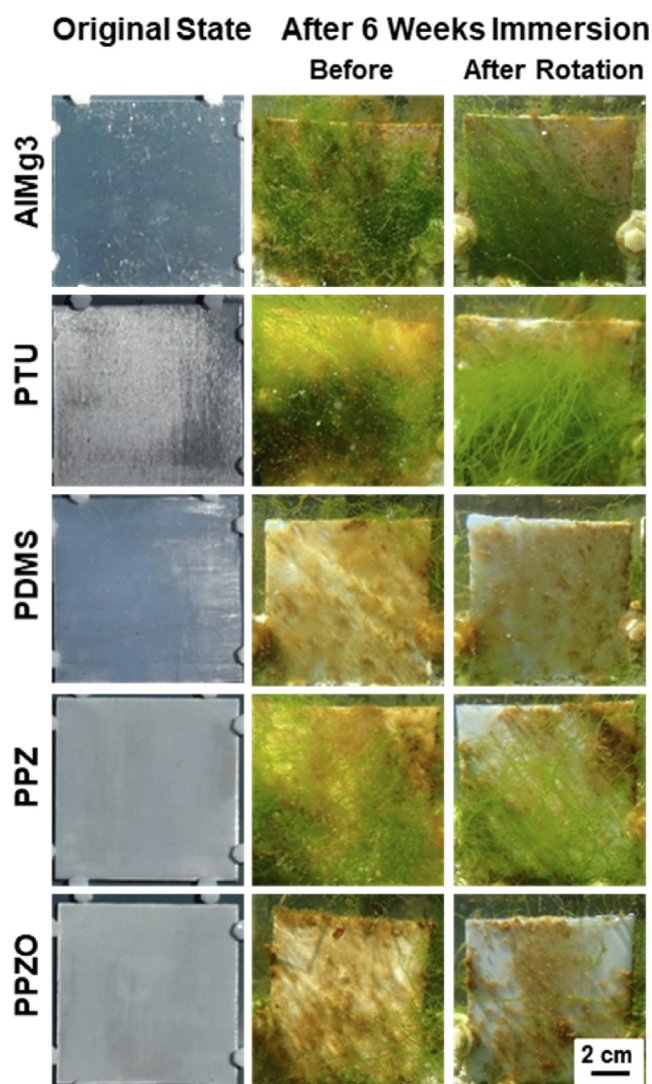


Fig. 7. Sample surfaces under dynamic biofouling testing in the Baltic Sea at Strande Harbor, Germany: AlMg3, PTU, PDMS, PPZ, and PPZO. First column: original state of samples surfaces before immersion. Second column: surfaces after 6 weeks immersion and before the sixth 30 mins rotation. Third column: surfaces after 6 weeks of immersion after the sixth 30 mins rotation. The magnification in all images is identical.

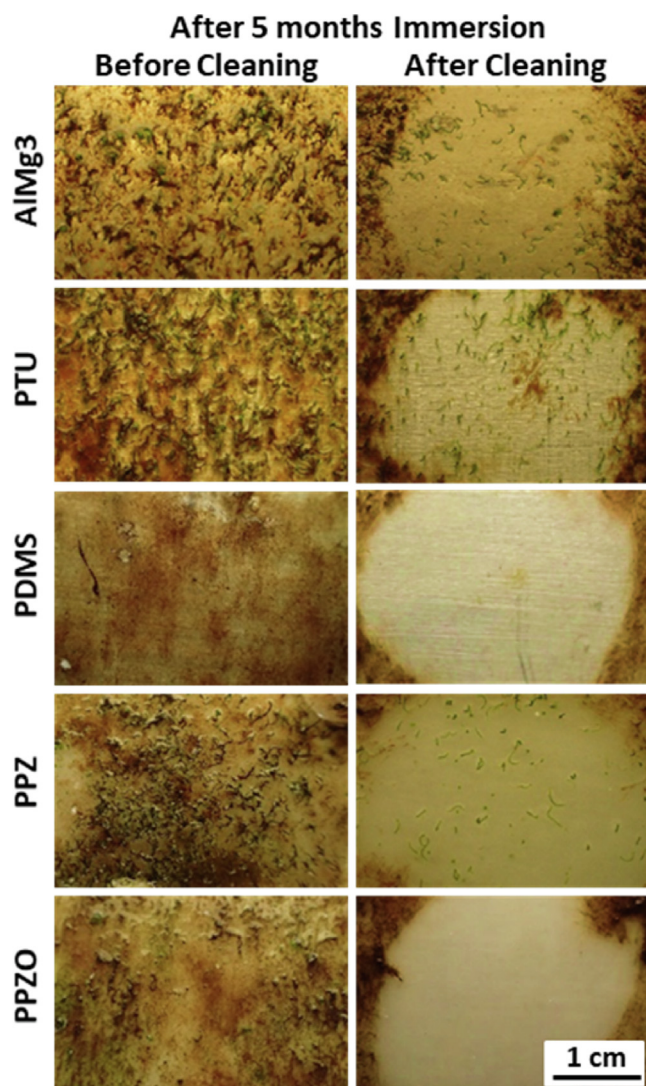


Fig. 8. Different substrates immersed in the Baltic Sea for 5 months before and after cleaning procedure: AIMg3, PTU, PDMS, PPZ, PPZO. The magnification in all images is identical.

tinues to search for a suitable settlement place, this pad is left behind on the surface. Once a suitable settlement area is found, the spores will be permanently attached by rapidly secreting N-linked, polydisperse, self-aggregating glycoproteins, thereby anchoring the spores to the surface [67]. Previously, PPZ nanocomposite showed a good fouling-release property in terms of barnacle adhesion due to the PDMS microdomain formation at the PTU/air interface [33,34]. However, the PPZ nanocomposite lacked biofouling control performance for algae prevention. This can be attributed to the hydrophilic PTU areas of around 100 μm between the PDMS domains on the PPZ surface. The zoospores are around 5–7 μm in length, and it was shown that the settlement of *Ulva* spores appears to be intensive on surfaces with a repeated topology pattern of 75–100 μm [64], making it possible to attach to PTU areas. Moreover, the secreted adhesive is a hydrophilic and gel-like material, which can cure to form a stiffer material with high cohesive strength on the hydrophilic PTU area of the PPZ surface [68]. For efficient prevention of algae attachment, a material should either deter its initial attachment or minimize the adhesion strength [43]. The deficient surface properties of PPZ were overcome by a thin layer of silicone oil on the PTU area of the PPZO surface. The influence of silicone oil on the prevention of algae adhesion can

be attributed to the water repellency (signified by the increased water contact angle) and the surface slippage [58].

In previous research, Ba et al. [49] developed silicone oil-modified PDMS coating and investigated the response of diatoms to the coating. The coating exhibited low adhesion and a high removal rate of benthic diatoms due to increased hydrophobicity, decreased elastic modulus, and prolonged time of silicone oil leaching of the coating. However, the long-term fouling release property of the coating needs to be evaluated in the field test. Moreover, the tensile strength of the coating was only around 0.3 MPa which is 200 times lower than the tensile strength of the PPZO nanocomposite developed in this study. Amini et al. [43] developed the same material system (i.e., silicone oil-infused PDMS) and investigated the response of mussels to such a surface. They demonstrated in laboratory and field studies that silicone oil-infused PDMS coatings significantly reduce mussels' attachment. It has been suggested that lubricant infusion deceives mussels' mechanosensing ability, inhibits adhesive threads' secretion, and decreases the molecular work of adhesion, leading to low attachment frequency and much lower attachment strength. The mechanical properties and adhesion to substrates of their coating need further investigation by the approach demonstrated in this study. Galhenage et al. [69] used a silicone-PU system for the incorporation of silicone oil. However, the results of the mechanical properties were not shown in their study. The attached algae in the field test could not be completely cleaned with a water jet (1.65 or 0.69 MPa). As a comparison, all attached algae on the PPZO surface were completely removed by a cleaning process with much lower pressure (20 kPa). Zhang et al. [70] fabricated a self-healing slippery organogel and investigated the bacterial attachment. This was done by infusing silicone oil into a PDMS-based polyurea matrix. The organogel showed good performance in inhibiting bacterial (*Pseudoalteromonas* sp.) attachment. However, the tensile strength of their developed coating was only around 0.15 MPa, which is 400 times lower than PPZO. Although after cutting the material into two pieces and putting them back in contact, a complete self-healing was obtained after 48 h at room temperature, the long healing time may limit its application. Ware et al. [71] mimicked the lubricating mechanism of the pitcher plant by fabricating nanostructured wrinkled surfaces from Teflon, polystyrene, and poly(4-vinylpyridine) and infusing silicone oil into the wrinkles. Infused surfaces inhibited the growth of *Pseudoalteromonas* spp. bacteria up to 99% and mitigated the attachment of algae in a 7-week field test. However, the application of such coatings in large scale is challenging. In comparison, the PPZO is suitable for large-scale application.

4. Conclusion

In summary, the present study demonstrates the fabrication of the PPZO nanocomposite, i.e., 1 wt% lubricant-modified PDMS/PTU nanocomposite reinforced with 1 wt% micro-nano t-ZnO particles, by a blending process, for environmentally friendly marine biofouling control applications. The incorporation of 1 wt% silicone oil vinyl300 had no relevant negative effect on the mechanical properties of the nanocomposite. The tensile strength of the PPZO nanocomposite was around 63 MPa. The adhesion strength of the nanocomposite to AIMg3 substrate was approximately 4 MPa, which was 30 times higher than that of pure PDMS. The PPZO nanocomposite showed good biofouling control property in the Baltic Sea under dynamic testing for five months. PPZO nanocomposites could significantly reduce algae attachment compared to the nanocomposite without silicone oil. The low amount of algae attached to the surface could be completely removed by gentle brush cleaning. The stability of silicone oil after the biofouling field

test and cleaning procedures was confirmed by confocal microscopy and Raman spectroscopy. Overall, the PPZO nanocomposite inherited not only favorable mechanical stability and adhesion strength to substrates originating from matrix material PTU but also promising biofouling control properties due to the formation of PDMS microdomains and presence of silicone oil at the PTU/air interface.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2022.110389>.

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