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Multifunctional coatings based on silicone matrix and propolis extract

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ABSTRACT

The development of new green alternatives for anticorrosive and antifouling coatings is essential for the conservation of the environment. A coating with more than one functionality, for example both anticorrosion and antifouling is of great interest for cost reduction and for improved coating efficiency. In this work, the multifunctional effect of propolis within a silicone matrix coating was evaluated. Fourier transform infrared (FTIR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) analyses confirmed the presence of several compounds with active properties (*e.g.* polyphenols, cinnamic acid, ferulic acid, and diterpenes). The addition of propolis and TiO_2 increased the thermal stability of the final coating while keeping the water contact angle of the silicone, near to 98°. Electrochemical impedance spectroscopy (EIS) experiments showed that the presence of propolis increased the anticorrosive properties, and bacterial experiments showed decreased adhesion of the gram-positive bacteria *Staphylococcus aureus* (ATCC 6538). Marine experiments also showed the excellent antifouling efficiency of the paint containing propolis over 11 months. The use of a natural pigment allied to a solvent free resin contributes to the formulation of more environmentally friendly paints.

1. Introduction

Coatings are the most suitable solution for protection against marine fouling and for corrosion control in ship hulls. The deterioration of metal structures – and consequently their failure – can occur due to corrosion in saline environments [1]. Biofouling contributes to metal degradation due to the substantial modification of the pH and aeration of the surfaces [2,3]. The presence of bacteria can also increase the corrosion rate; the presence of bactericidal coatings can minimise this problem [2,3]. Intensification of fuel consumption, due to the increase in the vessel weight and drag, are problems similarly related to the presence of biofouling [4,5].

Numerous solutions against corrosion, bacteria, and marine fouling have been proposed, but several of these compounds are extremely aggressive to the environment. Tributyltin (TBT) was used as a highly effective antifouling biocide, but its extremely toxic effect on marine fauna led to its ban in the early 2000s [6,7]. Several toxic herbicides, bactericides, and algaecides are still used in the formulation of commercial antifouling paints, perhaps their environmental impact is imminent [8,9]. In the past, chromates were employed in anticorrosive coatings, and gave excellent results against corrosion; however, hexavalent chromium has carcinogenic effects in humans and high toxicity for marine fishes [10].

New green alternatives against biofouling have been reported in literature [11–15]. Pranantyo et al. [14] developed an environmentally benign antifouling coating with hyperbranched polyglycerols, using bioinspired compounds such as tannic acid, to form an antifouling layer. Hölken et al. [15] proposed the use of ZnO with a two component polyurethane paint as an environmentally friendly antifouling coating. A recent review described the importance and the novelty of using sol-gel coatings as new alternatives against marine fouling [16].

Recent works concerning corrosion can also be found in literature. Naderi et al. [17] discussed the use of strontium aluminium polyphosphate as a green pigment in epoxy anticorrosion paints to avoid metal deterioration. Chen et al. [18] developed a self-healing coating with tung oil microcapsules. Darvish et al. [19] used zinc aluminium

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phosphate, an additive with low toxicity, in polyurethane paints for protection against the corrosion of metals. A list of natural corrosion inhibitors can be extensively found in the literature [20].

The use of polydimethylsiloxane (PDMS) coatings for antifouling purposes began commercially in 2006; this is an excellent alternative biocide-free antifouling paint [21]. The high durability and the low surface tension of the PDMS matrix make this component very interesting in combating the adhesion of marine fouling. The surface tension of PDMS film is around 20–30 mN/m, which represents the lowest degree of biological adhesion [22]. This makes antibacterial adhesive coatings formulated with PDMS an interesting way to combat bacterial settlement. The low surface tension of the silicone resin also makes this type of matrix interesting for corrosion applications [21].

Propolis is a complex mixture of resin, wax, pollen, and bee saliva, and is used by bees to form a hive in an antiseptic environment [23,24]. Its high antimicrobial and bactericidal activity make propolis the object of study for many researchers [25–27]. The chemical composition of propolis is dependent on the geographical localisation and season [28]. High amounts of polyphenolic compounds are identified including gallic, caffeic, fumaric, and cinnamic acids [28]. Dolabella et al. [29] reported the efficiency of using propolis extract as a corrosion inhibitor of mild steel. However, no work was found in the literature on the utilisation of propolis in coatings, especially those with multifunctional activities.

The aim of the current work was to study the antifouling and anticorrosion performance and the inhibition of bacterial adhesion of a solvent-free paint, formulated with silicone as a main polymeric matrix and propolis as a natural inhibitor additive. The coatings were tested against marine fouling in an outdoor environment, and against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria in controlled medium. The anticorrosion properties of the films were tested in a 3.5% (w/v) NaCl solution for a period of two weeks.

2. Experimental

2.1. Materials

Dry propolis (yellow powder with 0.24% of quercetin, batch SPOPVA0002A7/12, Delaware, Brazil)), TiO_2 powder (95% purity, 0.60 μm of average diameter, Polimeum, Brazil), PDMS SQ 8000/3.5 M (high purity, molecular weight of ~ 40,000, viscosity of 3000 cPs and colorless, Silaex, Brazil) and hardener Silicat 70 (Silaex, Brazil) were used in the preparation of the non-toxic bi-component coatings, which were codified as 'PPRO' and 'blank', for films with and without propolis, respectively. Additionally, a commercial antifouling coating, Micron® Premium (Akzo Nobel, USA), was used as a control for the antifouling activity tests in the marine environment, and was codified as the 'commercial' coating. Acrylic panels (20 cm × 15 cm × 0.7 cm) were employed in the marine tests. Carbon steel samples (0.105% C, 0.44% Mn, 0.16% Cr, 0.01% Cu, 0.01% S, 0.01% P; 5 cm × 5 cm × 0.8 mm) were used in electrochemical tests. Silicone discs (2 cm diameter, 0.8 cm thickness) were used for the bacterial analyses.

2.2. Preparation of the modified resin

The modified elastomer resin was obtained with a disperser Dispermat model N1 (WMA–Getzmann GMBH, Germany). Silicone was homogenised in the disperser for 15 min at 3000 rpm. Then, dry propolis and TiO_2 were added as pigments in the silicone matrix and dispersed for 30 min at 4000 rpm. The pot-life of this formulation after the addition of hardener is about 2 h. The coatings formulation is given in Table 1.

2.3. Marine fouling tests

The coatings were applied by brush and the average dry thicknesses (measured by Byko-7500 test unit, BYK Gardner, Germany) were: 300 ± 12 μm (blank); 280 ± 10 μm (commercial); and 325 ± 15 μm (PPRO). All samples were immersed in an open channel to Atlantic Ocean (29°58′35.5″ south, 50°07′23.0″ west) during 11 months at a depth of approximately 1 m, local with intense marine fouling in Brazil.

Table 1
Coatings composition.

Coating	Resin/ hardener ratio[a] (%)	Silicone + hardener (%)[a]	Propolis/ TiO_2[b] (%)	PVC[c] (%)
Blank	91:9	100	–	–
PPRO	91:9	76	23/1	50

[a] Mass percentage.
[b] Propolis/TiO_2 ratio (for each 23 g of propolis, 1 g of TiO_2 was added).
[c] Pigment volume concentration.

2.4. Corrosion tests

The electrochemical behaviour of the samples were determined by electrochemical impedance spectroscopy (EIS) using an AUTOLAB PGSTAT 302 N potentiostat coupled to a frequency response analyser. All measurements were performed in potentiostatic mode at the open circuit potential with an amplitude signal of 10 mV, and with frequencies ranging from 100 kHz to 0.10 Hz. The electrolyte used in the EIS measurements was a solution of 3.5% (w/v) NaCl. The area of the working electrodes (samples) was delimited by the electrochemical cell (2 cm^2). A saturated calomel electrode (SCE) was used as reference, and a platinum wire (spiral format) used as an auxiliary electrode.

2.5. In vitro bacterial adhesion test

Bacterial adhesion was performed with *E. coli* (ATCC 25,922) and *S. aureus* (ATCC 6538). At first, the samples (1.0 cm diameter, 0.3 cm thickness) were added in a falcon, with: 6 mL of bacterial suspension (approximately 10^7 colony-forming units (CFU/mL)); 6 mL of sterile water; and 3 mL of Tryptic Soy Broth (TSB) for *E. coli* or Brain Heart Infusion (BHI) for *S. aureus*; and then incubated at 37 °C for either 24 h or 7 days. In the 7-day experiment, 3 mL of the suspension was removed and replaced by 3 mL of fresh medium on the third day of incubation. After the incubation period (24 h or 7 days), the samples were washed three times in sterile saline, then transferred to a falcon containing 3 mL of saline and vortexed vigorously for 1 min. Finally, 0.1 mL of this bacterial solution was pipetted in a tube with 0.9 mL of saline, and serial dilutions were performed to determine the bacterial cell count. *E. coli* and *S. aureus* cell counting was used to compare bacterial adhesion between the blank (pure silicone) and PPRO coatings. Unpaired two-tailed Student's *t*-tests were performed for the statistical analysis ($p \leq 0.05$ was considered significant). All experiments were carried out at least three times.

2.6. Characterisation

Optical microscopy images were obtained using a Dino-lite model AD7013MT USB digital microscope. The Fourier transform infrared (FTIR) spectrum was recorded using a Perkin Elmer Spectrum 1000 spectrometer. Dry propolis was deposited on KBr disks and analysed in transmittance mode. FTIR spectra of blank and PPRO coatings surface were recorded using an FTIR 4100 Jasco spectrophotometer coupled with an attenuated total reflection accessory (Specac model MKII Golden Gate Heated Single Reflection Diamond ATR). Thermogravimetric analyses (TGA, TA Instruments TGA 2050) were performed in a nitrogen atmosphere at a scan rate of 20 °C/min. ^{13}C NMR spectra were performed using a 300 MHz Bruker AMX300 spectrometer operating at 75.5 MHz. The propolis sample was diluted in