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Incorporation of Natural Surfactants in Natural Resin-Based Coatings and Analysis of Rheological Behaviour to Obtain Natural Antifouling Agents

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Biofouling develops on the submerged surfaces of different structures, causing economic losses to local facilities. Marine-type biofouling causes problems such as reduced speed and increased fuel in vessels, as well as maintenance costs in submerged installations such as heat exchanger pipelines in thermoelectric plants. Anti-fouling coatings based on synthetic chemicals is the primary strategy for combating fouling in the marine industry. TBT-containing biocides (tributyltin) are effective in reducing scale but are vetoed for being harmful to other beings in the marine ecosystem in addition to target organisms. The development of new antifouling coatings relative to the marine environment is indeed crucial but requires certain characteristics to be designated as antifouling in marine environments, with the ability of slow erosion, low viscosity, high adhesion and maintenance of the coating over some important parameters. The objective of the present work was to evaluate some of the parameters of the area of paints and coatings of two biodegradable and erodible coatings, formulated with a natural resin containing natural surfactants to prevent biofouling. The evaluation of the quality of the formulated antifouling was done by tests of solids content by mass, visual aspect analysis and tack free touching. Since the formulation does not actually become an ink, adaptations of the protocols of the standards have been made. The solids content of the formulations was verified according to the methodology adapted from the Petrobras standard N 1367 (2008) and expressed in percentage by mass. Regarding the other tests, the visual aspect analysis was based on the Petrobras standard N 2630 (2011) and the tack-free touch-drying test, adapted from ASTM D 1640 (2014). The tests were performed in triplicate. The results obtained evidenced the interest in mixing these natural surfactants to obtain a promising coating with lower toxicity than traditional systems.

1. Introduction

Biofouling is a natural and cosmopolitan phenomenon that causes major economic losses, particularly in the marine economy sectors. However, the biofouling can cause serious ecological problems. Invasion of exotic species brought about by ballast water may occur. As well, attempts to eliminate and control biofouling cause the release of toxic components in the local biota and development of physiological problems in different aquatic organisms (Amara et al., 2018; Gule et al., 2016).

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These biofouling agents are represented by single and multicellular living beings such as bacteria, fungi, microalgae and macroalgae, even more developed organisms such as mussels and barnacles (Angeles and Flemming, 2009).

These organisms can attach themselves to natural surfaces such as rocks, woods, other animals, and man-made materials such as boat hulls, pipelines, oil rigs, or any other underwater surfaces (Gule et al., 2016; Yebra et al., 2004). Uncontrolled biofouling can lead to several damages to vessels such as damage to equipment, increased weight and fuel volume and hydroelectric and thermoelectric structural damage due to biocorrosion processes and clogging caused by reduced pipe diameter (Fitridge et al., 2012; Lekbach et al., 2018).

Marine-type paints and coatings are the most common practices to prevent biofouling. These types of protection incorporate antifouling compounds that prevent the development of biofouling (Yebra et al., 2004; Yebra and Weinell, 2009). With the ban on organotin compounds by the International Maritime Organization (IMO) since September 2008, there is an urgent demand for new antifouling compounds that do not cause environmental problems (Amara et al., 2018). Therefore, the exploration of effective and environmentally friendly antifouling compounds has become an urgent demand for the marine coating and similar industries (Ciriminna et al., 2015).

Marine coatings are designed to provide different performance characteristics such as corrosion protection; scale control; resistance to damage; chemical resistance; decorative effect among others (Yebra and Weinell, 2009). Although the main attribute of many coatings is not corrosion protection, it is important to recognize that coating degradation and failure, for example, will lead to conditions that result in corrosion of the steel substrate as well as the formation of biofouling (Ulaeto et al., 2017). Thus, when developing and evaluating paint performance, test methods that simulate actual use are always adopted.

In the paint industry, test method specifications are developed by national and international organizations such as the International Standards Organization (ISO) and the American Society of Testing Materials (ASTM). Quality control of paints and related materials in the industry is performed using fast-running characterization tests that respond to important ink properties (Yebra and Weinell, 2009). Normally, in Brazil, to standardize the analysis of tests on paints and related materials, ABNT standards are used and, in the absence of any regularization, ASTM standards are used. Evaluation tests of color control, viscosity, solids content, specific mass, pot life among others are used.

Surface active molecules (surfactants) constitute an interesting class of substances with unique structural characteristics such as the ability to bind to compounds of different polarities simultaneously. The properties of surfactants play significant roles in industrial and consumer products, including detergents, paints, paper products, pharmaceuticals and cosmetics (Dave and Joshi, 2017; Zhang et al., 2018).

As synthetic surfactants are produced from petroleum sources, over the past two decades, new surfactant molecules have appeared at a relatively fast pace as the search for less toxic substituents are needed (Almeida et al., 2017; Santos et al., 2016). As well as a growing interest in work involving the preparation and study of natural product-based surfactants (Pinto et al., 2018). Surfactants synthesized from natural raw materials are generally referred to as natural surfactants. Sugar fatty acid esters, fatty acid esters or amino acid amides belong to this category (Krister, 2001). The use of natural surfactants from raw materials from living sources has several advantages over synthetic surfactants such as biodegradability, specific activity at extreme temperatures, pH and salinity, low toxicity and selectivity (Santos et al., 2016; Sivapathasekaran and Sen, 2017).

Thus, the objective of the present work was to evaluate some of the parameters of the area of paints and coatings of three biodegradable and erodible coatings, already evaluated in recent studies by Silva et al. (2018), formulated with a natural resin and containing natural surfactants, obtained by chemical modification of soybean oil (*Glycine max* (L.)) with potential for application to a coating on submerged surfaces in seawater with the presence of biofouling.

2. Material and methods

2.1 Obtaining the natural surfactants from the residual soybean oil (*Glycine max* (L.))

The synthesis of natural surfactants was performed according to the methodology of Silva et al. (2018). The residual soybean oil (Glycine max (L.) was used as a source of fatty acids in the reactions. The monoglyceride glyceryl laurate was produced by direct esterification reaction through acid catalysis. Hydroxylated oleic acid was produced by the epoxidation reaction, followed by the opening of the epoxy ring in an aqueous medium. After obtaining the natural surfactants, they were kept under ambient conditions and incorporated at a rate of 2.5, 5.0 and 7.5% (w / w) for the formulation of each coating.

2.2 Preparation of the soluble natural resin-based coatings natural surfactants

The composition of the formulation (standard matrix) used as a base was adapted from Acevedo et al. (2013) and expressed in percentage by mass. The components from formulation were mixed in a mechanical agitator (Tecnal LTDA, Brazil) at 2000 rpm for 50 min. Thus, three natural resin-based paint compositions were prepared (Table I). Each paint was evaluated for viscosity, mass solids and pot life parameters.

Table 1: Soluble natural resin-based coatings formulated with natural surfactants to obtain antifouling

Mixture	Composition
Control	Matrix without active
Mixture 1	Matrix + glyceryl laurate
Mixture 2	Matrix + hydroxylated oleic acid

2.3 Standard tests for paints, coatings and varnishes based on ABNT standards used in this experiment

Since the formulation is not really an ink, adaptations of the standards protocols have been made. Each paint was evaluated for mass solids, pot-life and Ford viscosity parameters.

The solids content of the formulations was verified according to the methodology adapted from Petrobras N 1367 (2008). For this test different concentrations (2.5, 5.0 and 7.5%) of natural surfactants glyceryl laurate and hydroxylated oleic acid were added to the formulation. The test consisted of determining the percentage by mass of non-volatile paint components. Then, 2.0 g of each sample of triplicate formulated antifouling was weighed and then heated in an oven at 110 ± 5 ° C for 60 min. The oven samples were taken and left to stand for 15 min in a desiccator at room temperature and then weighed again. After the time fixed in the method and under the conditions described, the mass is determined and the solid content per mass obtained by the following expression (Eq1). The test was performed in triplicate.

$$\text{Weight (\%)} = (\text{dry film weight } (g) \,/\, \text{liquid paint weight } (g)) \times 100 \qquad (1)$$

Pot-life testing was performed according to ABNT NBR 15742 (2015) and consisted of the evaluation of the useful life of the mixture. The test followed with the measurement of viscosity soon after mixing (T0) of the formulation components and solvent and assessed its development over time (T) in weeks.

Ford viscosity is a major measure of the paint's rheological conditions, that is, its flow and application conditions. The viscosity of each formulation was determined with the aid of a Ford 4 Cup viscometer, whose liquid flow hole has a diameter of 4.12 mm ABNT NBR 5849 (2015). In order to determine the kinematic viscosity of the natural soluble resin-based coatings formulated, two 100 mL aliquots were initially removed, shaken and poured in turn at an average temperature of 25 ± 0.5 ° C and at the same time. With the aid of a digital stopwatch the flow time of each formulation was measured every 3 minutes. Following viscosity analysis, the two previously removed 100 mL aliquots were reinstated with the soluble natural resin-based coatings formulated. The test was performed in triplicate. Viscosity is the average of these values, expressed as s or $mm^2.s^{-1}$. The conversion from seconds to $mm^2.s^{-1}$ is given by the following expression (Eq 2), used for hole viscometer number 4.

$$\text{Kinetics viscosity} = (3.846 \times t) - 17.300 \qquad (2)$$

Where: t is the time, expressed in seconds (s).

3. Results and discussions

In Figure 1, the results of the mass solids content of the formulated mixtures are presented. Different concentrations (2.5, 5.0 and 7.5%) of natural surfactants glyceryl laurate and hydroxylated oleic acid were incorporated into the standard matrix to each formulation. However, there was no overall loss of solid content. Regardless of the presence of the natural surfactant, there was no interference in the matrix mass after removal of solvent by evaporation in an oven.

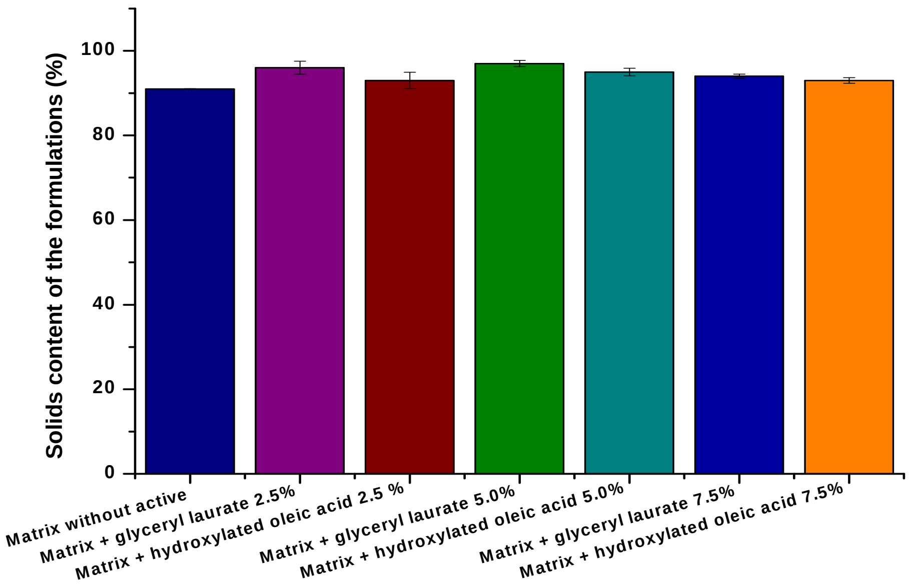

Figure 1: Percentages of the mass solids content of the formulated mixtures after removal of solvent by evaporation in an oven.

High solids content is important because it reduces the number of applications and produces coating with a larger coating layer and reducing the reapplication time of the protective layer.

In Table 2, shows the result of one week of the mix lifetime test. In this, we can observe that in this interval the kinetic viscosity of the mixtures did not present significant variation, however the highest values of kinetic viscosity were the compositions matrix + glyceryl laurate and matrix + hydroxylated oleic acid. This test determines how long the product can maintain its characteristics, in this case the viscosity, after the first contact with the atmosphere (Soliman, Mohamed and NaserGomaa, 2014).

Table 2: Pot-life analysis values after one week of testing. T_0 initial kinetic viscosity and T_7 final kinetic viscosity after seven days

Mixture	Composition	Initial kinetic viscosity T_0 $(mm^2.s^{-1})$	Final kinetics viscosity T_7 $(mm^2.s^{-1})$
Control	Matrix without active	54.85	57.45
Mixture 1	Matrix + glyceryl laurate	637.44	638.67
Mixture 2	Matrix + hydroxylated oleic acid	629.92	630.04

In Table 3, the compositions matrix + glyceryl laurate and matrix + hydroxylated oleic acid had the highest viscosities, 170 and 168 respectively. Possibly, the molecular and physical structure of the substances used as bioactive, in this case natural surfactants, which have different densities and masses influenced the viscosity response.

Table 3: Viscosity analysis values for different formulations

Mixture	Composition	Viscosity $(mm^2.s^{-1})$
Control	Matrix without active	18.76
Mixture 1	Matrix + glyceryl laurate	170.24
Mixture 2	Matrix + hydroxylated oleic acid	168.29

Soluble paints contain natural resin in their composition. The natural resin collected from various pine species, it is the most commonly used soluble binder component in various types of coatings. It is made up of about 85-90% acidic material and 10-15% neutral substances. Mostly it has a mixture of unsaturated diterpene monocarboxylic acids (C-20) (Finnie and Williams, 2010). The viscosity test indicates whether the paint is of the specified consistency and together with the determination of solids it is checked for a solvent loss during the mixing process. The content of solids in paint formulations, in general, influences the result of the product's viscosity, the higher the content of particles present, the greater the viscosity of the resulting fluid. In formulations containing natural surfactants, it was observed that there was an increase of more than 100% in viscosity compared to the control (matrix without active) (Table 3). Although high viscosity means less lick of paint, depending on the oxygenation of the environment this can be a problem. In this case, when observing the data from the pot-life test (Table 2), it is clear that the solvent used, and the product's maintenance conditions also influence viscosity. In the pot-life test the measurement of kinetic viscosity on the 7th day showed no differences, even after keeping them closed, after exposure to ambient air.

4. Conclusions

Given the results obtained there was no loss of solid material and the viscosity presented indicated that the formulation components were affected in some way by the presence of natural surfactants, as it made the formulation less fluid. The matrix + glyceryl laurate coating has so far presented the best quality for use as an antifouling coating. However, adaptations and improvements in the composition of this and the other formulations will be necessary to increase the treatment permanence time when exposed to adverse conditions such as those found in natural environments.

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