Original Article

Effect of Al₂O₃ particles on the adhesion, wear, and corrosion performance of epoxy coatings for protection of umbilical cables accessories for subsea oil and gas production systems

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Abstract

Umbilical cables accessories of subsea oil and gas production systems are exposed to very high mechanical stresses, abrasive wear, and continuous electrolyte action in submerged condition. Epoxy-based composite coatings with ceramic loading have been studied for providing protection to the accessories. By adding micro-Al₂O₃ particles to the polymeric matrix, the corrosion and wear properties are expected to be improved without a significant impact on the cost as compared with unmodified epoxy coating. In order to evaluate the tribological properties, adhesion and micro-scale abrasive tests have been performed on epoxy before and after loading of 26 vol.% micro Al₂O₃ particles. The results showed that wear resistance and adhesion to the substrate of ceramic-loaded epoxy increased by 30% and 50%, respectively. Electrochemical impedance spectroscopy tests were also performed and higher resistances of epoxy with ceramic loading were confirmed, which indicate a more efficient barrier against electrolyte permeation. In addition, coatings with thicknesses of 120 μm, 240 μm, and 360 μm were evaluated and the results showed that the resistances of both coatings increased with the increase in the thickness. Thus, the loading of micro Al₂O₃ particles into epoxy resin matrix increased its adhesion, wear, and corrosion resistances without significant impact on the cost, which renders the use of this coating in umbilical accessories feasible.

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1. Introduction

Epoxy resins are commonly used as coat for applications where corrosion protection is necessary owing to their high strength, high elastic modulus, strong bond ability, and
excellent chemical stability. However, characteristics such as brittleness and sensitivity to micro-cracks owing to their three-dimensional network structure, lower impact toughness, and poor fatigue property may restrict their applications [1]. To improve the wear resistance of polymers, various micro or nanoparticles of ceramic oxides have been used (Si$_3$N$_4$, ZnO, TiO$_2$, Al$_2$O$_3$, SiO$_2$, montmortilinite, etc.) [2–9]. This can be attributed to the high capacity of small particles to fill cavities. Moreover, other properties such as stiffness, impact energy, and failure strain are improved with the addition of alumina [10]. Smaller particles improve the properties of these materials because the absolute number of particles inserted in a fixed volume of charge is larger. Alumina nanoparticles also increase the adhesion strength of bonded steel with modified epoxy adhesive [11]. Nano Al$_2$O$_3$ particles may significantly improve the corrosion resistance of epoxy coatings. Nanoparticles reduce the water permeability of the coating and improve its resistance against hydrolytic degradation [12]. Nevertheless, some fillers can weaken the tribological and corrosion resistance properties owing to filler aggregation, leading to an increase of cracks across epoxy composite coatings [13].

This work aimed to study the adhesion, wear, and corrosion of both unmodified and modified epoxy coating used for the accessories of subsea umbilical cables.

2. Materials and methods

2.1. Materials

AISI 1020 steel was used as the substrate for all the coatings employed in this work.

2.2. Preparation of epoxy composites coatings

Prior to coating, the substrate surface was cleaned and prepared with Sa3 (ISO8501-1:2011) grade abrasive blasting with roughness profile between 50 and 80 µm for proper anchoring of the coating. The specification of the epoxy used was in accordance with the Petrobras standard (N-2680:2011), with a proportion of ten parts by volume of resin to one part of curing agent, with the addition of 26 vol.% Al$_2$O$_3$ microparticles to the specimens with modified epoxy. Three test specimens were prepared with the application of one, two, and three layers of 120 µm each with an airless sprayer with an interval of 12 h between each application, when applicable. The drying process was carried out in an oven isolated from humidity at room temperature.

2.3. Coating characterization

The coatings were analyzed using SEM and EDS to obtain the micrographs of the unmodified and ceramic-loaded epoxy coatings. The amount of ceramic load in the coating was measured using a semi-automatic granulometer image analyzer. The principle of operation of the program consists of intersection count of the phases with lines pre-established by the analyzer. In the present study, four horizontal and four vertical lines were distributed evenly in the images.

### Table 1 – Wear test parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load [N]</td>
<td>0.24</td>
</tr>
<tr>
<td>Specimen Inclination [°]</td>
<td>40</td>
</tr>
<tr>
<td>Ball tangential speed [m/s]</td>
<td>0.1</td>
</tr>
<tr>
<td>Ball material</td>
<td>Steel AISI 52100</td>
</tr>
<tr>
<td>Ball diameter [mm]</td>
<td>25.4</td>
</tr>
<tr>
<td>Abrasive mud particles</td>
<td>SiC</td>
</tr>
<tr>
<td>Abrasive mud fluid</td>
<td>Distilled water</td>
</tr>
<tr>
<td>Abrasive concentration [vol.%]</td>
<td>20</td>
</tr>
<tr>
<td>Feed rate [drops/s]</td>
<td>0.4</td>
</tr>
<tr>
<td>Test distance [m]</td>
<td>4-8-16-24-32-40-50-60-70-80</td>
</tr>
<tr>
<td>Coating thickness [µm]</td>
<td>360</td>
</tr>
</tbody>
</table>

Source: Author (2016).

2.4. Adhesion

The adhesion characteristic of each coating was analyzed using pull-off tests according to the standard (ASTM-D4541:2002). This test determines the maximum perpendicular force an area of the coating can withstand prior to its peeling, i.e., the adhesion tension of the coating to the substrate. The test equipment consists of a controller module (which controls the flow and pressure of the gas), flexible hose, detachment device, and traction pin. The test preparation consists of adhesion of the flat face of the pin to the coating. The top of the pin is screwed onto the detachment device, which receives pressurized gas from the controller module through flexible hoses. The glue used was 3M Epoxy Adhesive DP 460.

2.5. Wear

The rotating ball abrasive wear tests were performed using the abrasive material as an aqueous suspension. The concentration of the abrasive used in this work was 20% by volume, with 25 cm$^3$ of SiC (80 g, considering its density as 3.2 g/cm$^3$) in 100 cm$^3$ of distilled water.

The equipment used in the tests was the CSM Calowear, which has a load cell with digital display showing the force applied by the Ø25.4 mm ball to the specimen, shaft speed adjustment, test time limiter, cycle counter, and pump for dripping the abrasive mud. In addition, the equipment has a magnifying glass attached to a computer with software for measuring the surface diameter of the wear scar formed during the test. Table 1 lists the parameters used in the wear tests.

The wear scar diameter formed during the test is recorded in a spreadsheet, together with other test parameters (ball diameter, number of rotations, and load), where the equivalent distance S traveled by the sphere and the wear coefficient k are calculated, using the following equations.

\[ S = \frac{\pi Rt \cdot \mu \text{ball}}{\sqrt{(\frac{4}{3}) \cdot \text{ball}^3/4 - c^2}} \]  \hspace{1cm} (1)

\[ k = \frac{\pi b^4}{32 \cdot \mu \text{ball} \cdot SFN} \]  \hspace{1cm} (2)

where n is the number of rotations of the equipment shaft; R is the shaft radius; Ø$_\text{ball}$ is the ball diameter; b is the wear scar diameter; c is half width of the groove over which the ball is supported; F$_N$ is the load of the ball against the coating.
2.6. Corrosion

The electrochemical impedance spectroscopy tests were performed over the frequency spectrum from 40 kHz to 4 mHz, considering five points per decade, which is the range from $10^0$ to $10^{11}$ on the logarithmic scale, in a range of 10 mV. All the tests were performed at room temperature with 3.5% NaCl solution to simulate the conditions of the marine environment. The results were analyzed using Nova software (Metrohm Autolab).

The exposed area of the coatings was scratch-free and standardized with an area of 12.9 cm². Both unmodified and Al₂O₃-loaded epoxy coatings had the average dry thicknesses of 120, 240, and 360 µm. The objective is to evaluate the influence of addition of ceramic particles and the thickness variation of the coatings on the properties of the coatings. The electrochemical impedance tests were conducted at IFES corrosion laboratory and the electrochemical impedance plots were determined at exact intervals of 24 h in order to evaluate the behavior of the coatings over six days of testing.

3. Results and discussion

3.1. Coating characterization

On development of this work, the micrographs of unmodified epoxy and epoxy with ceramic particles were obtained using SEM/EDS analysis.

The amount of ceramic particles in the modified epoxy coating was measured using a semi-automatic granulometer image analyzer. The operating principle of this software, which has been developed by the Mechanical Engineering Department of Federal University of Espírito Santo (UFES), consists of the intersection count of the phases with lines pre-established by the analyzer. According to measurements, reinforcements in the polymeric matrix are 26.3 ± 0.3%, with particles size between 5 µm and 15 µm. Further, via EDS analysis, this reinforcement was observed to be composed predominantly by Al₂O₃, with residual concentrations of SiO₂ and TiO₂, as presented in Fig. 1.

![Table 2 – Results of pull-off tests on unmodified epoxy coating.](image1)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension [MPa]</td>
<td>19.4</td>
<td>21.0</td>
<td>20.4</td>
<td>20.7</td>
<td>20.4 ± 0.6</td>
</tr>
</tbody>
</table>

Source: Author.

![Table 3 – Results of pull-off tests on epoxy coating with Al₂O₃.](image2)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension [MPa]</td>
<td>37.1</td>
<td>27.0</td>
<td>28.1</td>
<td>28.4</td>
<td>30.2 ± 4.0</td>
</tr>
</tbody>
</table>

Source: Author.

3.2. Adhesion

The adhesion characteristics of the coating s were analyzed using pull-off tests. The results are presented in Tables 2 and 3.

When analyzing the test results of both coatings, it can be observed that there was an increase of approximately 50% of the adhesion value of the coating to the substrate when Al₂O₃ particles were added to the epoxy resin.

This increase in the adhesion of the ceramic-loaded epoxy resin coating was expected, as it is well known that the addition of ceramic microparticles to the surface coatings contributes significantly to the increase of the adhesion to the substrate, in addition to other properties such as hardness, wear resistance, and corrosion resistance [14–16].

Micrographs of unmodified epoxy (Fig. 2a) and epoxy with ceramic particles (Fig. 2b) show coating microstructures after adhesion tests, where it is possible to see how the inclusion of particles decrease the voids and pores, improving the adhesion of coating to the substrate as consequence. It is also possible to see some particles detachment due to failure on the coating.

The results of the adhesion tests of this work converge with the results obtained in [17], where pull-off tests were carried out following the same standard of this work (ASTM D4541) in unmodified epoxy coatings and with the addition of three types of ceramic nanoparticles: CaCO₃, SiO₂, and Al₂O₃.
The results showed that the addition of particles to the epoxy improves its adhesion to the steel substrate significantly. The axial bond strength of unmodified epoxy to the steel substrate increased from 4 MPa to 12 MPa owing to the addition of CaCO$_3$ and SiO$_2$, and to 18 MPa owing to the addition of Al$_2$O$_3$.

The results of this work also converge with those of [11], where pull-off tests were carried out in epoxy by varying the amount of Al$_2$O$_3$ nanoparticles. The results showed that the proportion of Al$_2$O$_3$ nanoparticles influences the epoxy adhesion, and the adhesion increases with the increase in the amount of nanoparticles.

These results can be associated with the physical characteristics of the ceramic filler, which improve the quality of epoxy resin matrix, reduce its porosity, and improve its adhesion, thus changing the physical and chemical properties of the substrate and coating interface [13].

### 3.3. Wear

Table 4 presents the average values of the wear coefficient for coatings with unmodified epoxy resin and epoxy resin with the addition of Al$_2$O$_3$.

It can be observed that there was a decrease of 30% in the wear coefficient of the epoxy resin coating when Al$_2$O$_3$ particulates were added to the polymer matrix.

This decrease in the wear of the ceramic-filled epoxy resin coating was expected, as the addition of ceramic microparticles to surface coatings tends to contribute significantly to the wear resistance, in addition to other properties such as adhesion, hardness, and corrosion resistance [18].

Micrographs of unmodified epoxy (Fig. 3a) and epoxy with ceramic particles (Fig. 3b) show coating microstructures after wear tests, where it is possible to see how the inclusion of ceramic particles reinforces the polymeric matrix, making the coating more resistant as consequence.

The addition of inorganic particles to epoxy resin improves the mechanical properties of the coating, such as adhesion,
hardness, modulus of elasticity, and wear resistance [19–22]. This increase in wear resistance can be associated with the dispersion of the particles in the polymer matrix, which reduce the wear depth, rendering the surface more resistant to wear [13].

3.4. Corrosion

Impedance tests were performed for all the coatings studied under full immersion. The deterioration kinetics of each coating was characterized using resistance and capacitance graphs as a function of test time. These data were extracted from the impedance diagrams. The values were determined considering that the impedance diagram was characterized by a capacitive arc, according to Nyquist representation, as presented in Fig. 4.

Eq. (3) was used to calculate the impedance resistive component (R). Accordingly, the coordinate in the real axis of the impedance (Zr) corresponding to the maximum point of the graph (Re_max) was considered. This value was multiplied by two and the result was subtracted from the electrolyte resistance (Re), which is generally given as the first resistance measure of the electrochemical impedance diagram.

$$ R = (2Re_{\text{max}}) - Re $$

In addition, these results were parameterized with the value of the exposed area of the coating, which was 12.9 cm². The maximum frequency points used for the capacitance calculations were highlighted in the impedance graphs. Using this value of resistance (R), the capacitance (C) was calculated, according to the formula:

$$ C = (2\pi f_{\text{max}} R) - 1 $$ (4)

where $f_{\text{max}}$ corresponds to the frequency of the maximum point of the impedance diagram.

With these considerations, the electrochemical impedance diagrams were determined at exact intervals of 24 h in order to evaluate the behavior of the coatings over the six days of testing. The impedance diagrams were analyzed to compare and discuss the influence of the addition of ceramic filler to the epoxy resin and the influence of the variation of thickness of each coating.

The impedance diagrams of the 120-μm-thick, 240-μm-thick, and 360-μm-thick coatings are shown in Fig. 5a–c, respectively.

The electrochemical impedance results for the epoxy coatings with Al₂O₃ were evaluated for six days of immersion. The impedance diagrams of the 120-μm-thick, 240-μm-thick, and 360-μm-thick Al₂O₃ epoxy coatings are summarized in Fig. 6a–c, respectively.

In the case of unmodified epoxy coatings (Fig. 5) and ceramic-loaded epoxy coatings (Fig. 6), a classical behavior can be observed [23]. This behavior indicates that, for small immersion times (up to 20 days), only a capacitive arc is detected and the size of this arc decreases with the passage of time. For a better visualization, the diagram was enlarged in the upper right corner of each figure, showing the decrease of capacitive arc until the sixth day of immersion.

An equivalent electric circuit for the interpretation of the results illustrates that the capacitance and resistance are related to the coating and the impedance corresponds to the occurrence of the faradic processes at the coating/metal interface. According to the proposed circuit, at the initial stages of the corrosion test, the sample exhibits the behavior of an ideal capacitor. In addition, the capacitance of the sample increases, whereas the resistance tends to decrease, owing to the permeation of water and aggressive ions, which initiate the corrosive
process when they come into contact with the metal/coating interface [18].

When evaluating the results of the two coatings separately, it can be observed that the resistance increases as the thickness increases from 120 μm to 360 μm. Splengen et al. [24] reached the same conclusions when evaluating the results of electrochemical impedance tests on epoxy coatings of thickness 15 μm, 50 μm, 100 μm, and 140 μm, demonstrating that high thicknesses guarantee low permeability of electrolyte.

Furthermore, the results of the impedance tests of unmodified epoxy samples are compared with the results of the epoxy with Al₂O₃ filler. Higher strength is observed in filled epoxy coatings for all three thicknesses. This proves that the addition of Al₂O₃ particles in these proportions improves the electrochemical properties of the coating, rendering the permeation of the electrolyte difficult.

The higher resistance of the samples with ceramic loading can be attributed to the filling of small cavities and the increase of specific surface area owing to the inclusion of the microparticles [12]. This is because the electrolyte permeates more easily through the voids or pores of the coating [23].

Thus, the addition of microparticles hinders the permeation of the electrolyte through the coating. In other words, the microparticles act as an additional or denser barrier against corrosive solutions. The particles reduce the porosity of the coating, rendering the permeation of the electrolyte to the substrate difficult [13].

These results suggest an increase in the corrosion resistance and hydrolytic degradation of coatings with the addition of alumina microparticles. This is because the small size and large total surface area of these particles result in a decrease in the number of paths for the diffusion of the corrosive electrolyte through the coating [12].

According to the criteria adopted for analyzing and obtaining the data of the impedance diagrams presented in Figs. 5 and 6, Eqs. (3) and (4) were used to calculate the (a) resistance and (b) capacitance presented in the graphs of Fig. 7, indicating their variations over the test time.

It can be observed in Fig. 7a that the resistance of both unmodified and ceramic-filled epoxy coatings decreased over the test time.

It can be observed in Fig. 7b that the capacitance of the coatings increased throughout the test, except for the capacitance of the unmodified epoxy coating of thickness 120 μm, which exhibited slight fluctuation.

As described in previous works, if the protection mechanism is via a barrier, the capacitances tend to increase with the immersion time, which is usually associated with the absorption of electrolyte inside the coating with consequent increase in the dielectric constant. However, the passage of electrolyte through the coating toward the metal can leach species that

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Fig. 6 – Impedance diagram of epoxy coating + Al₂O₃ of thickness (a) 120, (b) 240 and (c) 360 μm.
Source: Author, 2016.

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Fig. 7 – (a) Resistance and (b) capacitance of the pure and Al₂O₃ epoxy coatings over six days of test.
Source: Author, 2016.
promote its passivation and/or introduce structural changes in the film [16]. In these cases, even a decrease of the capacitance can be observed, according to the behavior shown in Fig. 7b.

Although there was a significant decrease of the coating barrier effectiveness as immersion time increases, no change was detected on coatings microstructure from the first to the last day of test, as this type of corrosion test does not result in visual damage on samples in short term.

The graph of Fig. 8 illustrates the comparison of coatings properties evaluated in this work. Notably, all the properties (corrosion resistance, wear resistance, and adhesion) are improved with the addition of the Al2O3 filler to the epoxy. A gain of corrosion resistance is also observed with the increase in the layer thickness of both unmodified and ceramic-filled epoxy coatings. Costs are calculated considering the raw material, equipment, and inspection hours required to coat an umbilical accessory. As inspection costs are very high, both coatings have virtually the same cost. The main factor that increases the costs of coatings with the increase in the thickness is the need to apply more coats. As the curing time of each coat is approximately 12 h, the process lasts several days, thus significantly increasing the inspection costs.

In general, the results of this work suggest that both coatings, with and without ceramic load, with the three thicknesses employed can provide good anticorrosion protection to the steel substrate. This is because coats with resistance of approximately $10^8$ Ω typically provide excellent protection against corrosion whereas coats with resistance of approximately $10^6$ Ω promote poor corrosion protection. In this study, the resistances obtained were between $10^8$ Ω and $10^{11}$ Ω.

Notably, the electrochemical impedance technique is a powerful tool for obtaining information from the system under study. However, its results may have complex interpretations and may also be influenced by defects in the samples. Hence, to achieve good reproducibility of results in electrochemical tests, homogeneity in the preparation of the samples is a key part of the process, with particular attention to coating thickness and surface preparation. In addition, it is necessary to use complementary techniques for the correct analysis of the study material.

These techniques used for the evaluation of anticorrosive coatings include corrosion tests, complementary electrochemical measurements, accelerated tests, water vapor permeability tests, and adhesion tests. The natural exposure tests represent the closest mechanisms of the ideal for the coatings, but they have the disadvantage of requiring long periods of analysis, rendering them unviable sometimes.

4. Conclusions

In this work, the influence of the addition of Al2O3 micro particles to the matrix of epoxy resin was evaluated. Two types of epoxy coatings were applied on steel substrate-unmodified and with the addition of Al2O3 micro particles. In addition, these two coatings were applied with three different thicknesses – 120, 240, and 360 μm – in order to evaluate the influence of the thickness on the properties of the coating.

The addition of approximately 26 vol.% micro Al2O3 particles has increased the adhesion of the coating to the substrate by 50%, as compared with unmodified epoxy, from 20.4 MPa to 30.2 MPa. This result can be explained by the decrease of voids and pores in the coating due to inclusion of micro particles, which improves the coating adhesion to the substrate.

The addition of approximately 26 vol.% of micro-Al2O3 particles increased the wear resistance of the coating by 30%, as compared with unmodified epoxy, decreasing its wear rate from $4.2 \times 10^{-11}$ to $2.9 \times 10^{-11}$ m²/N. This result can be explained by the reinforcement of the polymeric matrix by the inclusion of ceramic particles, which improves the coating resistance.

Electrochemical impedance tests were also carried out, whereby it was concluded that the addition of Al2O3 particles in these proportions improves the electrochemical properties of the coating, rendering the permeation of the electrolyte difficult, increasing the resistance and thus providing greater corrosion protection to the coating. In the same impedance tests, it was observed that thicker coatings have higher resistances.

Nevertheless, the coatings with the lowest thickness have acceptable resistance values, according to literature. Therefore, it would be interesting in economic terms to evaluate the feasibility of reducing the coatings thickness in the accessories, via more electrochemical tests associated with complementary tests, such as natural exposure and accelerated corrosion tests, as it would be possible to reduce the amount of coating and time of execution and inspection.

Conflicts of interest

The authors declare no conflicts of interest.
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References