Mechanical effort of ceramic particle-reinforced epoxy matrix used as a sealing layer on aluminum coatings by Arco Spray

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Abstract. The coating against the corrosion and wear of carbon steel with pure aluminum applied by thermal projection with electric arc (arc spray) presents a porous surface. This is the reason why adding a sealing with a polymer layer, regularly epoxy is necessary. However, epoxy-based sealing solutions usually do not have high performance against abrasive wear. In this research a new product has been developed in composite material with polymer matrix (PMCs), epoxy paint reinforced with ceramic particles, in order to improve the performance of this layer against abrasive wear. Preliminary runs were made with 3 variables: Epoxy matrix (2 types: epoxy S and epoxy C); Size of reinforcing ceramic particles (two levels: 1 µm 9 µm) and percentage of ceramic reinforcement (4 levels: 0%, 20 %, 33.3% and 50 %). Adhesion and abrasive wear tests were performed to show that the composite material with epoxy matrix type C, has better performance than the composite material with epoxy matrix type S. Increasing the percentage of reinforcement particles showed that the composite material with type C epoxy matrix maintained high levels of adhesion to the aluminum layer and showed an increase in abrasive wear resistance by about 60% compared to the resin without reinforcements.

1. Introduction
In recent years, surface treatment and corrosion control in structures is an issue that goes beyond protection and conservation, including in immersion materials such as: boats, ships, boats, tugs, barges, stilts, dock pilings, pipes and underwater platforms [1] metal coatings with Aluminum, Zinc and combinations thereof have proven to be a very good alternative for corrosion protection given the double protection of these metals, by barrier and by cathodic protection is also a clean, emission-free production that does not contaminate the environment . Worldwide, the coating with aluminum by Thermal Projection with electric arc is replacing the paints; However, the problem of abrasive wear, although improved with respect to paints, is an unresolved problem. During the last two years, a group of researchers from the Simon Bolivar University have worked and researched the optimization of aluminum coating, in order to achieve the double performance of the deposited layer against wear and corrosion [2] . Despite the high initial cost of applying aluminum coating, with arc spray technology, compared to high-performance paint coating, the group of researchers managed to estimate that the cost of the life cycle in 21 years of a Caribbean fuel transfer barge, coated with aluminum, is about 40% of the cost when coated with paint, and maintains structural integrity by extending its lifespan, while with painting processes at the end of the cycle in 21 years will be very deteriorated [3], this is due to the pores and conduction pathways that occur through the shrinkage of the coating during the curing process, causing the ease of corrosive electrolyte penetration into the film and access to the metal interface /
coating [4]; along with the effects of low draft rubbing on the rivers in the shipping sector, therefore a naval device coated with aluminum with the arc spray technique, will generate in the long term greater profitability, reducing maintenance costs [5].

The surface of aluminum coatings and composite materials with aluminum matrix applied by arc spray, are porous and require a sealing layer that covers such pores and maintains high corrosion resistance, usually sealing is performed with a layer of epoxy paint, but this does not perform high against abrasive wear.

According to a study aimed at the industrial applications of composite materials at a university in Caracas, Venezuela, the development of a coat of paint, "wash primer" which is used to generate a high resistance to corrosion and wear, increasing the life of the device by approximately 27 years; exposing it to a harsh environment, where corrosion and wear have little significance when exposed, it is also determined that once its contact with water is not consecutive, it recovers with the time it stays away from it [6]. Other studies have shown that the mechanical behaviour and wear of epoxy compounds, reinforced with particles such as Al, Ti, C, Si and Al₂O₃, depend on the size of particles, the percentage of reinforcement and the preparation of the mixture [7] [8], in addition to identifying the appropriate type of polymer matrix, is very important for obtaining a good composite material. Among the most commonly used are the Epoxy resins, Polymethylmethacrylate and Polyeterimide [9].

In order to improve corrosion resistance, paints with high solid content have been developed; and its application requires an optimal coating design [10], for which a thorough analysis of the application process must be carried out; these advanced coatings allow good adhesion and extensive wear resistance, and are also made for specific ambient conditions and thus take advantage and achieve an optimal coating and be able to reduce costs for the mechanisms to be coated [11] [12].

This article presents the results of a preliminary study of the mechanical performance of new sealing products, developed by the GEMAS group of the Simon Bolivar University, made of composite material with reinforced polymer matrix (epoxy paint) with micro ceramic particles to increase wear performance in the shipping and maritime sector [13].

Two types of epoxy paint, red epoxy (S) and an epoxy with high solid (C), were used as a matrix; as a reinforcement, a high hardness ceramic powder was used in two particle sizes and in three percentage concentrations. Two types of mechanical tests were carried out after the specimens were obtained: adhesion, by the "pull off" method and to abrasive wear by the "pin on disk" method [14] [15], which serve as the basis for the development of new products in composite material for the Aluminum sealing by arc spray that ensure better performance as a solution to simultaneous wear and corrosion problems, mainly in the river shipping sector.

2. Materials and Methods

2.1. Materials.

In this study, two epoxy primers were used as a matrix of the composite coating reinforced with ceramic particles for the sealing of aluminum obtained by electric arc, one in red (referred to as S) and one in grey color (referred to as C), the latter with high aluminum metal solids. As a reinforcement, mixtures of metal oxides (Al, Ti and Zr) were used sifted with granulometry of 9 µm. As a substrate for the application of sealing in composite material, 80 mm x 80 mm specimens, with thickness of 3,175 mm (1/8 inch), coated with a layer of 200 µm of pure aluminum by arc spray were used, figure 1.
2.2. Methodology.

An experimental design is developed with two variables, one type of epoxy paint in levels (S or C) and the other the percentage of ceramic reinforcement in four levels (0%, 25%, 33.3% and 50%) see table 1, with two output factors that are: the degree of abrasive wear (see table 2), from the loss of layer thickness in the "pin on disk" (see figure 2 - (b)), as per ASTM G99-04 test and adhesion to the aluminum substrate (see table 3), evaluated by the "pull off" (see figure 2 - (a)), as say as per ASTM D4541. 4 replicates were made for each combination with a total of 12 specimens for each type of test.

The pin on disk test used a load of 2 N, abrasive paper No 600, rotation frequency of 342 RPM, turning radius 30 mm and the time that is limited by the thickness of the composite material, was estimated from a preliminary test, for this case with a thickness between 100 µm and 200 µm, the time taken was 30 s. Then, with a micrometer, the initial thickness of each sample is measured.

Using the ASTM G99-04 method, the procedure is performed to determine the wear of the materials using the pin on disk equipment, figure 2-(b), the thickness is measured again and the results tabulated in table 2 are obtained. Unreinforced epoxies are called (S-0) and (C-0), the following nomenclature is used to identify each specimen in composite material: the letter indicates the type of epoxy primer, the first number of ceramic particles in µm, and the last number is percentage of reinforcement in the matrix (see table 1). figure 2, shows the equipments used for this investigation.

| Percentage of reinforcement | Epoxy resin |   |
|-----------------------------|-------------|---|
| 0                           | S – 0       | C – 0 |
| 20                          | S-9-25      | C-9-25 |
| 33,3                        | S-9-33      | C-9-33 |
| 50                          | S-9-50      | C-9-50 |

Figure 2. Tests (a) Pull off adhesion and (b) Abrasive wear "pin on disk".
3. Conducting the experiment

Figure 1 shows the sequence of application of the two layers, (a) the base layer of 200 µm aluminum by arc spray on carbon steel A-36 to white metal, (b) and (c) the sealing layers with the composite materials obtained in the project. The mixtures of the ceramic reinforcement with the epoxy primer were made in parts by volume and dispersed by mechanical agitation in the hands of being applied with paint gun. They were dried in the environment for 48 hours before being cut with abrasive discs for laboratory testing. For each combination of variables, according to the experimental design 4 double-layered specimens were made, which were sectioned according to the test to be performed; for the wear test were obtained specimens of 1 cm² taken away from the edges, for the adhesion test the dimensions were 40 mm × 80 mm.

3.1. Experimental results

3.1.1. Abrasive wear testing

Table 2. Results. Pin on disk wear tests. Epoxy C and S reinforced with 9 µm ceramics.

| Epoxy C | Thickness loss (mm) | Average value | Error |
|---------|---------------------|---------------|-------|
| Specimens P1 | P2 | P3 | P4 |
| C- 0 | 0,10 | 0,11 | 0,08 | 0,09 | 0,10 | 0,011 |
| C-9-25 | 0,05 | 0,07 | 0,06 | 0,06 | 0,06 | 0,007 |
| C-9-33 | 0,04 | 0,03 | 0,04 | 0,03 | 0,04 | 0,005 |
| C-9-50 | 0,03 | 0,03 | 0,04 | 0,03 | 0,03 | 0,004 |

| Epoxy S | Thickness loss (mm) | Average value | Error |
|---------|---------------------|---------------|-------|
| Specimens P1 | P2 | P3 | P4 |
| S- 0 | 0,10 | 0,12 | 0,11 | 0,11 | 0,11 | 0,007 |
| S-9-25 | 0,10 | 0,05 | 0,06 | 0,05 | 0,07 | 0,021 |
| S-9-33 | 0,07 | 0,05 | 0,06 | 0,05 | 0,06 | 0,008 |
| S-9-50 | 0,06 | 0,07 | 0,09 | 0,06 | 0,07 | 0,012 |

Figure 3. Wear Intensity Graphics Vs% Of Ceramic Reinforcements.
3.1.2. *From the adhesion test.* Table 3 shows the results of the adhesion tests by the "Pull off" method with the two epoxy paints as the matrix of the composite material. The adhesion values of each specimen represented by $P_i$ are obtained from the average of three tests according to standard; The final mean value represents is the result of the 4 replicas.

| Epoxy C | Pull Off Adhesion (Psi) | Error | Observation |
|---------|-------------------------|-------|-------------|
| Specimens | P1  | P2  | P3  | P4  | Average value | |
| C-0     | 980,6 | 879,0 | 990,4 | 979,0 | 957,3 | 45,4 | Cohesive |
| C-9-25  | 986,0 | 821,0 | 688,0 | 845,0 | 835,0 | 105,7 | Cohesive |
| C-9-33  | 750,3 | 710,8 | 680,0 | 740,1 | 720,3 | 27,4 | Cohesive |
| C-9-50  | 545,0 | 571,0 | 560,0 | 571,3 | 561,8 | 10,7 | Cohesive |

| Epoxy S | Pull Off Adhesion (Psi) | Error | Observation |
|---------|-------------------------|-------|-------------|
| Specimens | P1  | P2  | P3  | P4  | Average value | |
| S-0     | 601,2 | 580,7 | 595,7 | 593,0 | 592,7 | 7,5 | adhesive with actuator |
| S-9-25  | 425,0 | 422,1 | 425,0 | 426,5 | 424,7 | 1,6 | adhesive with actuator |
| S-9-33  | 134,0 | 134,6 | 138,0 | 137,4 | 136,0 | 1,7 | adhesive with actuator |
| S-9-50  | 123,0 | 125,2 | 121,8 | 124,8 | 123,7 | 1,4 | adhesive with actuator |

![Adhesive resistance Vs Percentage ceramic reinforcement](image)

**Figure 4.** Adhesion test graphs (Psi) Vs the percentage of reinforcement.

Figure 5 shows some visual inspection images of tested specimens using the "Pull off" method, allowing you to determine whether the fault is adhesive, cohesive or mixed.
3.1.3. SEM/EDX analysis results. Figure 6(a) shows the three layers of a C-50 specimen, the base of carbon steel, then the middle layer of around 100 – 120 µm of aluminum per arc spray and the top layer thickened around 300 µm are shown. Some surface defects are noticed because it was manually paired where the gun did not give the required thickness; in real practice should not appear.

![Figure 6](image)

Figure 6. (a), (b) and (c) Images with different magnification obtained by SEM from a C-50, (d) Spectrun specimen obtained by EDX showing the peaks of Aluminium and oxygen of aluminium oxide shown in Figure 6 (c).
In images 6 (b) and (c) the high concentration of ceramic particles with good adhesion to the epoxy matrix is shown; there are also some pores. In Figure 6 (d) the spectrum obtained by EDX from the micro-analyzed ceramic particle in Figure 6 (c) shows the presence of alumina, with 79.35% Al by weight and 20.65% O by weight.

4. Discussion
Analysing mechanical performance, abrasive wear resistance and adhesion to the aluminum substrate, sealing layers with unreinforced epoxy matrix (S-0 and C-0) show that the red epoxy (S-0) without reinforcement has lower adhesion and less abrasive wear resistance than grey epoxy (C-0) as shown in figures 3 and 4. The use of these epoxy primers reinforced with ceramic particles of 9 µm, makes them a composite material with better performance against abrasive wear, in figure 3 it can be seen that with the increase of % reinforcement, the mechanical performance of the composite material is improved, being more relevant in the grey epoxy of high solids in metallic aluminum. According to the results obtained, it is observed that the worn thickness was reduced from 100 µm (without reinforcement) to 30 µm with a 33.3% reinforcement during test time: the increase to 50% reinforcement showed no significant change from 33.3%, indicating that attention should be paid to the interval 30% and 35 % of reinforcement to further investigate this material and analyse the rest of the properties of interest, such as resistance to bending, shock and adhesion.

The increase in the percentage of reinforcement, as expected, reduces the adhesion of the sealing layer, for this reason a maximum reinforcement limit must be found that guarantees improvements in wear resistance without detriment of the adhesion and without sacrificing resistance to impacts and mild bending of the substrate, the latter two properties have not been evaluated in this work. Figure 4 shows that in the grey epoxy (C) reinforced with ceramic the adhesion is maintained with high values with an increase of 50% reinforcement; for 33, 3% reinforcement the adherence was in the order of 560 Psi. The adhesion of the S compound turned out to be very low falling below 200 Psi for 33.3% reinforcement. AS illustrated in Figure 5, in the case of red epoxy (S) all failures in the adhesion test were of the cohesive type, indicating lack of cohesion inside the coating; in case of grey epoxy (C) all faults are mostly adhesive between the compound and the actuator, which shows strong adhesion between the aluminum and the sealing layer.

5. Conclusions
The study of the mechanical performance of the ceramic particle-reinforced epoxy matrix composite material has been carried out using two types of primers and three levels of reinforcement with an average size of 9 µm. The following conclusions are reached.

There is a significant difference in mechanical behavior between the two used epoxide primers, red (S) and grey (C), both unreinforced and reinforced with ceramic particles, being superior adhesion and resistance to abrasive wear of epoxy grey with high solids in aluminum metal, specially designed for porous aluminum sealing.

With the increase in the percentage of reinforcement both epoxies showed increased performance against abrasive wear and loss of adhesion to the aluminum substrate. Interestingly, these effects are interesting in grey epoxy, whose intensity to abrasive wear with reinforcements between 33% and 40 was reduced by 60% compared to the case without reinforcement, maintaining high levels of adhesion to the substrate. The adhesion values between grey epoxy and aluminum deposited by arc spray could not be specified, as more than 95% of the failures in the "pull off" test occurred between the actuator and the coating.

In general, a composite sealing product can be achieved with an epoxy matrix reinforced with ceramic particles with medium size of 9 µm, with a significant increase in abrasive wear resistance with reinforcement in the order of 33% and above, maintaining high levels of adherence to the substrate; above 33% reinforcement there was no significant increase in abrasive wear resistance, with no evidence of significant impact on adhesion to the aluminum substrate.
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