Characterization of Al/Polymer Composite Coating for Mechanical and Adhesion Properties on Steel

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Abstract. The purpose of this project is to carry out the development of a duplex aluminum/polymer coating for protection of steel structures deposited by thermal spray, in order to decrease the effects of corrosive atmospheres, by protecting the metallic surface from the aggressive atmospheres, and avoiding surface wear by erosion. In this work, a characterization of tensile properties Al/polymer composites, such as tensile modulus and tensile strength were carried out. The experimental work comprised the mixing of Al and polymer (medium density polyethylene – MDPE) powders in a "y" shaped mixer and the making of standard tensile composite specimens in an injection-molding machine for evaluation of their tensile properties in a tensile testing machine according to ASTM D638. Al/polymer composites were also applied to prepared steel surfaces by hot pressing and in the near future, by thermal spraying. The adhesion of these coatings to the substrate was evaluated according to ASTM C633. In the thermal spray process, difficulties concerning the use of polymers were found due to its low melting point, which caused a premature degradation of the polymer. Alternatives to overcome this problem such as the use of the HVOF (high velocity oxy-fuel) process, in which the particle dwell time in jet is lower are being investigated.

Keywords. duplex coating, thermal spray, polymer, aluminum, corrosion

1. Introduction

Among the factors that influence corrosion at low temperatures in petroleum transformation process, the flow velocity and turbulence are determinant, once they act as corrosion process accelerators. For instance, the velocity has leading effect in transfer lines corrosion, due to the high turbulence, mainly when caused by physical barriers, such as curves, excessive welding, misalignment and pumps.

The reduction of these effects is of great importance in industry, since when the pipeline life is increased and costs with maintenance and repairs decrease. So, the need of protection against corrosives atmospheres or better performance lead to a wide coating research area, mainly in polymeric coatings.

The purpose of this project is to carry out the development of a low friction duplex aluminum/polymer coating for protection of steel ducts, in order to eliminate or reduce the superficial conditions, which constitute physical barriers, being also a preliminary study of this application in the petroleum industry.

The polymeric coatings contribute to protection against localized corrosion (barrier), once they avoid the contact between the oil and the metallic surface. Besides this, they may reduce turbulence due to their low friction coefficient, which will help reducing erosion wear and corrosion.

The application of these coatings can be done by thermal spray, using nitrogen as carrier gas to minimize polymer degradation.

The polymer selection for this application must consider their abrasion resistance and friction behavior, polymer hardness and its adhesion to the substrate. However it is also important to evaluate its melting point and structure, which affect the polymer degradation rate and the coating mechanical properties. Therefore, polymers such polyurethanes, which have excellent abrasion resistance, have been used in such coatings, despite its high friction coefficient when compared with Teflon, for instance. The epoxi resins have good hardness and are excellent coatings, although the use of thermoplastics (PTFE, PE, PP, nylon, ABS, etc) can be economically attractive and offer even lower rugosity.

In this work an evaluation of aluminum/PEMD coating will be carried out, since the polymer is tip and of easy manufacturing, its low weigh and low water absorption. Such coatings will be deposited by thermal spray onto steel specimens, with and without substrate pre-heating.

2. Al/Polymer coatings deposited by thermal spray

Polymeric coatings are being used in a raising number of applications, including protection of surfaces against corrosion, wear and whether conditions, as said by Rajamäki et all (2000). At present, many coatings applications deposited by the thermo spray process are known. However, the use of polymers in coatings has limitations in some application, such low scratch resistance, poor adhesion to metallic substrates and high permeability. Therefore, many ways to get over these problems have been developed, such blends and polymer modifications. Another way to overcome such limitations is the use of high performance polymer and composites. The use of metal-polymer composites guarantees physical and mechanical properties better than the composites matrix's one. Polymeric matrix composites in coatings are interesting due to the mechanical properties conferred. The dispersion of metal, its alloys and ceramic particles increases the coating properties such tensile strength and high temperature resistance. Nevertheless, there must exist an adequate control of added material quantity, due to the rate of oxidation of the polymer during spray. It has been show that Fe-B alloy and aluminum powders added to the polymeric matrices of LDPE lead to an increase of 1.2-1.3 times in wear resistance of thermal spray coatings, as compared with a non-filled polymeric coating, as in Borisov et all (1998). In this project, still in development, one intend compare the performance of coatings prepared with Al/MDPE composites or cold mixtures of Al/MDPE powders.

One of the most used classes of polymer used in coatings is the polyolefins. Among them, the polyethylene (PE) and the polypropylene (PP) are one o the most used. And, in spite of the polyolefins advantages such easy processing, low price, low weigh and low water absorption, difficulties still exist. The chemical inertia of these polymers leads to a poor interaction with another materials such glass, metals and the majority of polymers.

For the polyethylene, however, these difficulties can be overcome by the chemical modification of this polymer. For PE, one can also notice that the polymer density has a determinant effect in its physical and mechanical properties. The increase in density of the PE leads to an increase in mechanical properties such tensile strength, stiffness, and hardness. Also melting point, chemical resistance and resistance to diffusion of gases and vapors increase when the density and the crystallinity increase. At the same time, as in Rajamäki et all (2000), impact resistance and resistance against environmental stress cracking decreases. For HDPE, the low flowability of particles during spray is also a problem. This problem can be controlled adding products that change the powder flow, as it occurs with the PE used in rotational molding.

The porosity of PE coatings can also be critical. It raises significantly with an exaggerated substrate pre-heating. It happens concerning gases formation inside the coating, caused by the polymer burning. So, during spray, if one has an adequate control of the substrate temperature, the degradation of the polymer will be lower and hence, the coating resistance will be higher [Rajamäki et all (2000)].

3. Thermal Spray

Thermal spray consists of a group of processes that allows the deposition of layers of metallic or non-metallic materials onto a previously prepared surface, in order to guarantee desired properties to the coated structure.

In these processes of thermal spray, the materials are melted or heated by a heat source generated in the gun's nozzle, through gases combustion, electric arc or plasma gas. Immediately after fusion, the material finely atomized is accelerated by compressed gases against the surface to be coated, reaching the melt or quasi-melt state. As the particles hit the surface, they flat and adhere to the base metal and, in sequence, to the previously flatted particles, forming the coatings that can contain oxide inclusions and pores.

The thermo spray process tem has been focused due its low cost, low investment capital and absence of shape and size of substrate, coating thickness and in site application limitations. The thermo spray process is commonly used with metals, alloys and low melting point ceramic materials. However, the use of polymers in this process has increased recently, according to Lugscheider et all (1998).

Another thermal spray process, which appears as a promising option for polymer coatings application, is the HVOF (high velocity oxy-fuel), that uses high-pressure carrier gas and high particles projection velocities. Dense and uniform polymeric coatings can be obtained with this process, controlling the particles dwell time in jet and the substrate temperature. Twardowski et all (2000) said this process showed an excellent solution for polymeric matrices nanocomposites and high performance thermoplastics deposition.

Polymers are low melting point materials and suffer decomposition at considered low temperatures (melting and decomposition points under 500°C). The flame temperature is much higher than the decomposition point, which induces the macromolecules degradation by oxidation chemical reactions, carbonization and polymeric chains breaking. Nevertheless, selecting the optimized process parameters, it is possible to obtain a degradation minimization. The parameters in the thermo spray process can be divided in groups: powder properties, flame characteristics, feed rate, distance between gun and substrate and substrate preparation. The powder properties such particles size, particles size distribution and particles shape have determinant effect over the feed in flame as well as in fusion and/or in polymer degradation rate, according to Twardowski et all (2000). Nitrogen as carrier gas minimizes the polymer degradation, yet protected by aluminum.

All these parameters influence, in some way, coatings properties, but the most important of them is substrate preparation.

As it is well known, adhesion to substrate is one of the most important coating properties. The best way to guarantee a good adhesion is an adequate surface preparation.

The surface must be activated so that, the melted projected particles, at the impact's moment, anchor to substrate and remain without residual impurities. The preparation consists of abrasive blasting and substrate pre-heating.

The adhesion mechanisms require a clean surface, exempt of rust, oxide crusts, grease, oil and of humidity. The cleaning patterns (Sa2; Sa2.5; Sa3) are reached through abrasive blasting, which eliminates the problems above commented.

Besides cleaning the substrate surface, the abrasive blasting assures the required surface rugosity so that the sprayed material anchor to substrate satisfactorily, since the abrasive material particles, when hitting the substrate with high velocity, pull out the surface material, causing irregularities and favorable anchorage points.

In synthesis, abrasive blasting has as purpose to clean the surface and facilitate mechanical anchorage.

Immediately done after the coating deposition, the surface pre-heating idea is to proportionate the grease, oil and humidity retained on surface, burning and volatilization. A reducing flame of the spray gun can do this pre-heating so as an independent equipment or an induction heating, when the substrate size is adequate. Pre-heating still favors internal stress elimination and therefore the layer adhesion and cohesion. When the particles hit the substrate, there is a quick cooling followed by a deposited material contraction and a small substrate swelling as it absorbs the particles kinetic energy. The flame heat hinders a good adhesion.

However, there is an ideal substrate pre-heating temperature for each material to be deposited, once if the substrate temperature is too much high, it can burn the polymer, producing gases inside the coating and a porosity rate increase. Consequently, the ideal temperature is determined in process optimization, said Twardowski et all (2000).

4. Experimental procedure

Three mixtures of aluminum and PE powder, with different weight fraction for each component: 30%Al and 70%PE, 70%Al and 30%PE and 50% each were prepared. The total mass of each mixture was 200 g and the powders were mixed in a "y" shaped mixer. Table (1) shows some properties of the used polymer.

Table 1. Polyethylene properties

Property	ASTM method	Value
Melt flow index (2,16kg/190°C) (g/10min)	D 1238	4.2
Density (g/cm^2)	D 792	0.935
Yield strength (MPa)	D 638	17
Rupture strength (MPa)	D 638	22
Elongation (%)	D 638	1.080
Flexure modulus (MPa)	D 747	450
Izod impact strength (J/m)	D 256	160
Softening point Vicat (°C)	D 1525	116

Six carbon steel specimens (150x80 mm) 8 mm thick and six 1.5 mm thick were prepared. The thinner specimens are to be used in bend tests and the thicker ones in metallographic examination. The surfaces were all prepared by abrasive blasting, prior to thermo spray process, with the different mixtures. One mixture was used for each par of thin and thick specimens. Substrate pre-heating was carried out in some specimens to evaluate its influence on coating quality, as compared to the coatings deposited without pre-heating.

Composites of Al/PE were also prepared in a injection-molding machine, at 180°C – 200°C depending on the composition. The samples were prepared according to standard tensile strength tests specimens (ASTM D638).

Al/polymer composites were also used to coat steel surfaces by hot pressing. The steel surfaces were submitted to an abrasive blasting in order to improve the anchorage of the coating to the substrate. The mixtures were pressed at about

200°C on standard cylinders for the coatings adhesion evaluation, according to ASTM C633-79 tensile test, showed in Fig. (1).

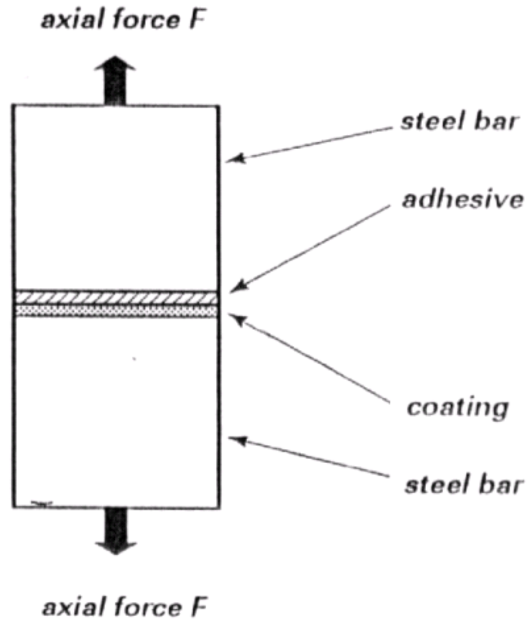

Figure 1. ASTM C633-79 tensile test

5. Results

To evaluate the PE behavior and predict its behavior when deposited by the thermo spray and HVOF processes, the morphology of the mixture with the higher aluminum content after compaction and heating in an oven (200°C) was studied. It was concluded that not only porosity was low but also, the mixture were homogeneous, according to Anjos at all (2003).

During the thermal spray process, some difficulties were found with the powder flowability inside the spray gun. The mixture retained humidity, which agglomerated the powder particles, so that the mixture could not reach the gun's nozzle. However, the problem was overcome by drying the mixture in an oven at 80°C prior to use. The lack of humidity allowed good powder flowability. Although the minimum drying period was not evaluated, drying was found to be extremely important for the process.

Another difficulty was that the polymer, when passing through the spray gun's nozzle, burnt and stuck to the gun, obstructing the flow of the mixture, due to its low degradation temperature. Thus, it was not possible deposit the coatings through this technique up to now. Therefore, since we do not dispose of the thermal spray gun to test further process conditions, the HVOF process will be tested. This attempt may be valuable since the particle dwell time in jet in this process is lower than in the thermo spray process preventing the particle degradation and hence, the obstruction of the gun's nozzle. Furthermore, in this process, the mixture passes through the flame, which has a uniform shape, which allows a uniform heating, avoiding excessive heat absorption.

Concerning the composites tensile strength tests, it may be concluded in Tab. (2), that the aluminum did not reinforce the chemically unmodified polymer, as expected, once the composites strengths obtained were lower than the strength of the pure polymer.

Table 2. Composites mechanical properties obtained by tensile strength tests.

Composite	**Rupture strength (MPa)**		**Elongation (%)**		**Young's Modulus (GPa)**	
	Average	**Standard Deviation**	**Average**	**Standard deviation**	**Average**	**Standard Deviation**
70% MDPE	9,4	0,4	21,2	4,2	0,8	0,18
50% MDPE	8,8	0,3	2,6	0,8	2,1	0,22

It was not possible to prepare the 70%Al composite through injection molding due to the high brittleness of the material.

Table (2) and Figs. (2) and (3) show that the addition of aluminum particles reduces significantly the materials toughness, enhancing its brittleness and therefore, acting only as unreinforcing filler. This result may be seen as a consequence of a poor adhesion in the aluminum/polyethylene interface. The MDPE composites tensile strengths are lower than the pure polymer strength, as shown in Tabs. (1) and (2).

In order to overcome this difficulty, we intend to use maleated polyethylene in our mixtures. This polymer will be modified through the reaction of maleic anhydride and MDPE in a reactive injection process. We expect that the use of modified MDPE will improve the adhesion in the Al/polymer interface, resulting in a reinforced material.

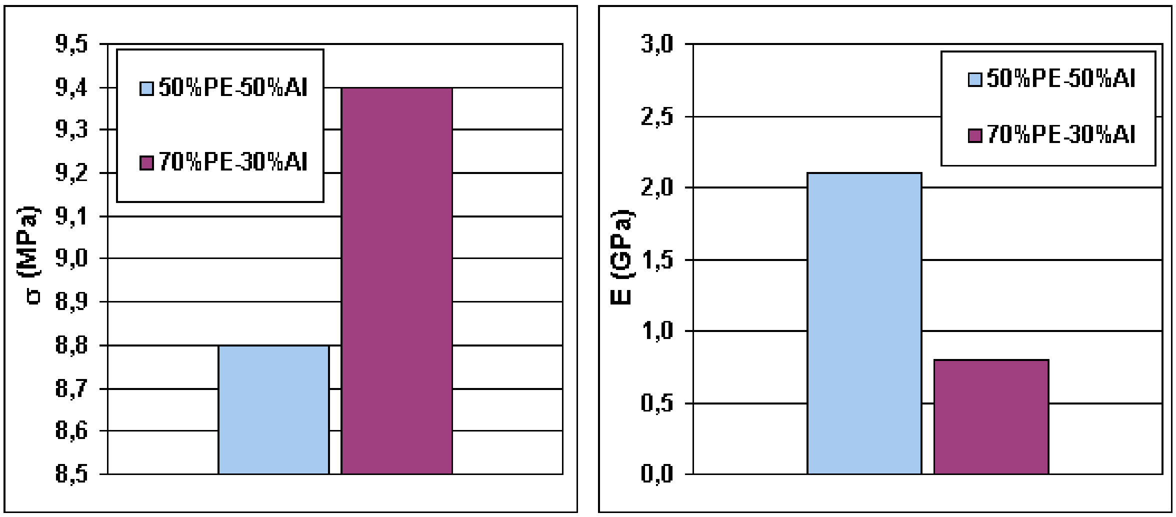

Figure 2. Composites mechanical properties

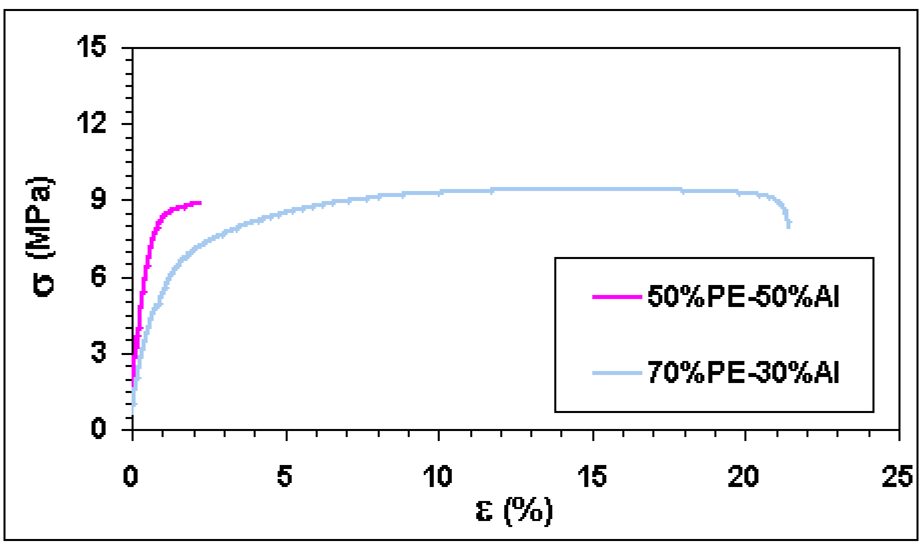

Figure 3. Tensile stress versus specific deformation curve for the prepared composites

Concerning the coating obtained by hot pressing, the coating film with the higher aluminum content could not be formed due to the low polymer content.

The used epoxy adhesive had little compatibility with the coating material and therefore a more suitable adhesive is still to be found. Therefore, instead of using the adhesive prior to the test, two cylinders were joined directly by the coating material through hot pressing. The other mixtures were analyzed this way and the tensile x strain curve (Fig. 4) and the obtained results are shown in Tab. (3).

Table 3. Coatings adhesion

Coating composition	**50% PE – 50% Al**	**70% PE – 30% Al**

Adhesion to substrate (MPa)	2,20	1,87

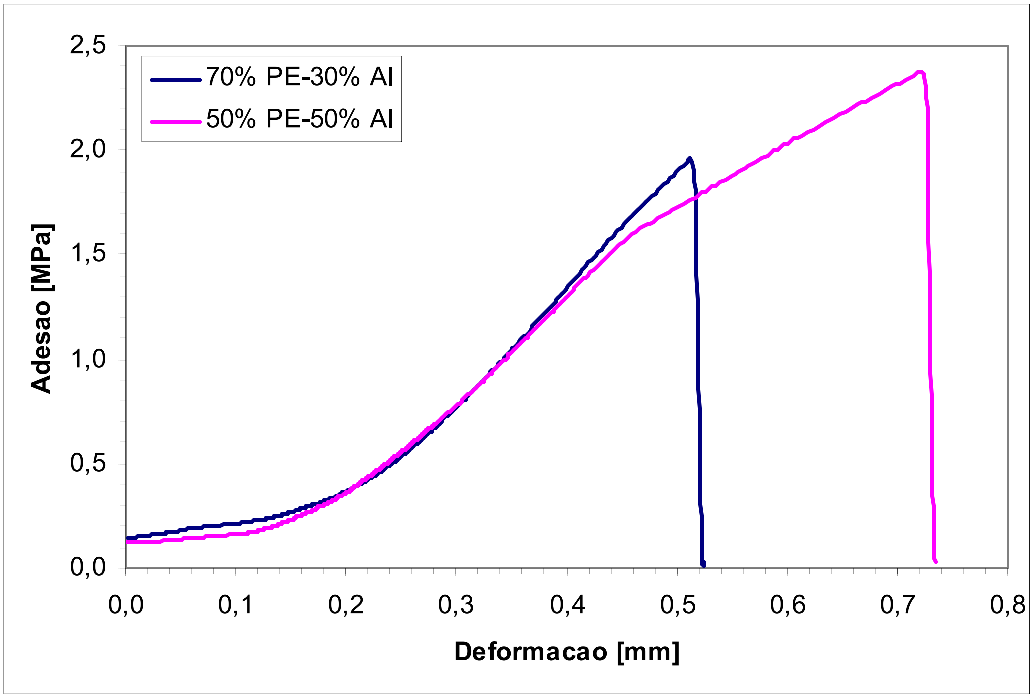

Figure 4. Tensile x strain behavior of the tensile test for both coatings composition

The shown results indicate that the specimens with higher aluminum content adhere more strongly to the substrate (steel). At the end of a particular test, the composite film appeared intact, even because the applied stress is still very low (around 2 MPa).

Figure (5) shows photographs obtained with an optical microscope (100x) of the different coated specimens. Although the films do not contain apparent pores, dispersion is not homogeneous and aluminum particles tend to aggregate. This level of dispersion is, however, not very different from what is observed in other particle composites.

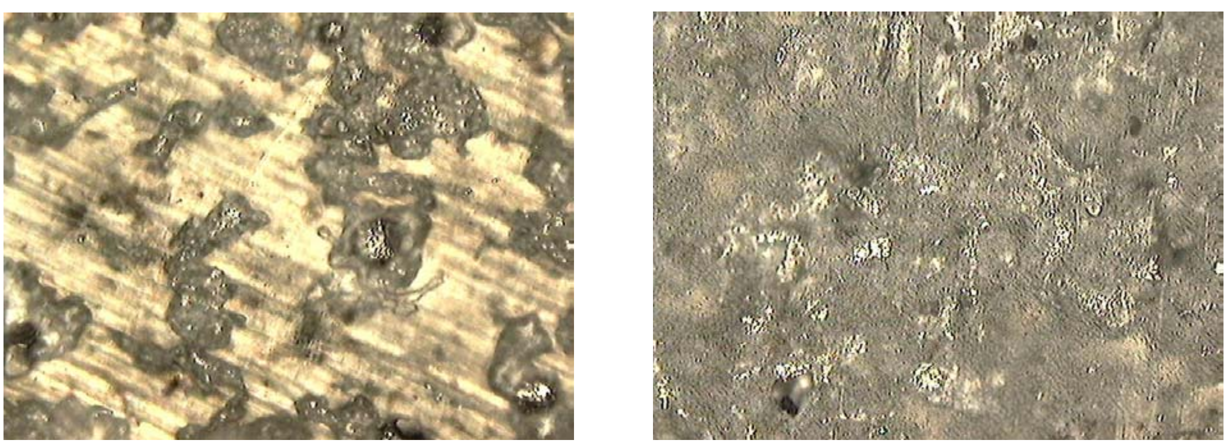

Figure 5. Morphologies of the 70% PE and 50% PE coatings respectively

The deposited films may be an indication of what is to be expected of the thermal spraying of the mixtures, once it can be done successfully, although due to the very different depositing mechanisms distinct results may be found.

6. Conclusions

Initial technical problems of the thermo spray process have been minimized through drying of the of the Al/polymer mixtures, although further investigations concerning the process parameters must be tested. Nevertheless, preliminary results indicate that the porosity, a main property of the deposited coatings as barrier against corrosion, may be minimized.

The addition of aluminum particles in the unmodified polymer did not reinforce the plastic, as expected. However, it was a useful mean to explore the hot pressing technique and adhesion evaluation, prior to the use of chemically modified PEMD.

7. Acknowledgments

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8. References

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