A PRELIMINARY INVESTIGATION INTO THERMAL SPRAY AND OTHER METAL/POLYMER DEPOSITION PROCESSES AND THEIR POTENTIAL USE IN THE OIL INDUSTRY

G. V. M. Anjos,
T. H. D. Sydenstricker,
R. S. C. Paredes and
S. C. Amico
Universidade Federal do Paraná
Setor de Ciências Tecnológicas
Departamento de Engenharia Mecânica
Caixa Postal 19011
Centro Politécnico
Bairro Jardim das Américas
81531-990, Curitiba, Paraná, Brasil
gustavomaximo@hotmail.com
thais@demec.ufpr.br
ramon@demec.ufpr.br
amico@ufpr.br

ABSTRACT

Polymeric coatings are being used in a raising number of applications, contributing to protection against weather conditions and localized corrosion, also reducing erosion wear. The coatings may be deposited by various processes and thermal spray is being recently investigated as a new alternative. This paper reports an exploratory study into various polymer deposition processes and evaluates their influence on the quality of the produced coating, concerning dispersion, cohesiveness and adhesion onto steel substrates. Different content aluminum/MDPE (medium density polyethylene) mixtures and processing parameters were studied as an attempt to identify the most promising parameters regarding their future application to produce coatings for the oil industry. The material characterization was carried out via mechanical testing (ASTM D638). The coating adhesion was evaluated by bend and ASTM C633-79 tensile tests. A microscopy evaluation of the coatings was also carried out. The produced films showed low friction surfaces and adequate adhesion to steel substrates. The presence of MAN (maleic anhydride) in the composite was responsible for the MDPE to recover its ductility, with a small increase of strength and rigidity, as well as a significant enhancement of coating adhesion to substrate.

Keywords: composite coating, thermal spray, aluminum/polymer

INTRODUCTION

Among the factors that influence corrosion at low temperatures (near room temperature), flow velocity and turbulence are determinant, since they act as corrosion accelerators. The velocity has a leading effect, for instance, on the corrosion rate in transfer lines, due to high turbulence mainly caused by physical barriers, such as curves, excessive welding, misalignment and pumps.

The reduction of these effects is of great importance for this industry, because if pipeline life is increased, maintenance and repair costs decrease. Therefore, the need for protection against corrosive atmospheres or better performance leads to a wide research area into coatings. Coatings are usually applied to enhance surface resistance against friction, fatigue, wear, and corrosion, being widely used since the 50´s.

Polymers are a common use class of material for coatings, being used in a raising number of applications, contributing to protection against weather conditions, localized corrosion (barrier) by preventing the contact between oil and metallic surface, they may also reduce turbulence due to their low friction coefficient, and as a consequence, reducing erosion wear and corrosion. The low friction coefficient of polymers allows their application between two sliding hard surfaces, resulting in cost minimization and contributing to the reduction of environmental impacts from the generation of solid residues (Rajamäki et al., 2000).

The polymer selection must consider its abrasion resistance, friction behavior, hardness and adhesion to the substrate. Moreover, it is important to evaluate its melting point and structure, which affect the polymer degradation rate and the coating mechanical properties. Examples of polymers include polyurethane (excellent abrasion resistance) and epoxidic resins (good hardness), although the use of thermoplastics (PTFE, PE, PP, nylon, ABS, etc) can be economically attractive and offer even lower rugosity.

According to Custódio (2002), PET and EMAA coatings have shown low friction coefficient and good adherence to the substrate, where high load was necessary to cause coating unpeeling in scratch testing. In fact, from the vast choice of polymers available nowadays, only a small number of them have been used as coating and, more specifically, literature data regarding the behavior of polymeric particles during thermal spray are scarce (Zhang et al., 1997).

Major polymer limitations include low scratch resistance, poor adhesion to metallic substrates and high gas permeability. The drawbacks of using polymers as coatings have been dealt with by using blends and modified polymers (Custódio et al., 2002), high performance polymers and composites (Lugscheider et al., 1998).

The use of metal-polymer composites aims to achieve a combination of physical and mechanical properties better than those of a single material (Silva et al., 1996), being possible to achieve good barrier and mechanical properties.

The dispersion of metals, their alloys or ceramic particles enhances coating properties of plastics such as tensile strength and high temperature resistance. In fact, Borisov (1998) shows that the addition of Fe-B alloy and aluminum powders to LDPE polymeric matrices lead to an increase in wear resistance of thermal spray coatings, as compared with a non-filled polymeric coating. Nevertheless, there is an optimal amount of added material, regarding the rate of polymer oxidation during spray.The deposition of these coatings can be carried out by thermal spray using nitrogen as carrier gas to minimize polymer degradation. This recently growing area (Borisov et al., 1998) is an alternative deposition process which does not require curing time, as in traditional multi-layer painting processes, being adequate to components and big structures, which cannot be held in polymeric suspensions (Brogan, 1996).

Thermal spray consists of a group of processes that allow the deposition of layers of metallic or non-metallic materials onto a previously prepared surface to guarantee desired properties to the coated structure (Petrovicova and Schadler, 2002).

During thermal spray, the materials are heated and/or melted by a heat source in the nozzle of the gun, generated by gas 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 flatten, adhering to the base metal; following layers adhere to previously deposited particles, constituting the coating, that may contain oxide inclusions and pores.

The thermal spray process requires low investment, is of low cost and does not impose restrictions regarding shape and size of the substrate, coating thickness and in-loco application. Recently, a variant of the traditional thermal spray process, HVOF (high velocity oxy-fuel), that uses high-pressure carrier gas and high particle projection velocities, has shown to be a promising option for high performance thermoplastic deposition (Twardowski, 2000; Petrovicova, 2000), producing dense and uniform polymeric coatings and minimizing polymer degradation since the mixture passes through a regular shape flame, which allows a uniform heating and avoids excessive heat absorption.

Nevertheless, one has to always bear in mind, that polymers are low melting point materials and undergo decomposition at low temperature (usually smaller than 300°C). The flame temperature is much higher than the polymer decomposition point, which induces degradation (Duarte et al., 2003) by oxidizing chemical reactions, polymeric chain scission and carbonization, evidenced by, for instance, the presence of bubbles in the coating.

Critical process parameters, such as powder properties (Twardowski et al., 2000; Yan et al., 2003), flame characteristics, feed rate, substrate preparation and distance between gun and substrate, must be carefully selected for each polymer to ensure complete fusion and minimum flame particle degradation (Brogan, 1996; Brogan et al., 1996). All these parameters influence, in some way, coatings properties, but perhaps the most important of them is substrate preparation, which has a crucial impact on adhesion coating/substrate (Shiflett et al., 2001).

The substrate surface must be activated so that, the melted projected particles anchor, at impact, to the substrate and remain without residual impurities. The usual preparation consists of abrasive blasting and substrate pre-heating. Abrasive blasting eliminates rust, oxide crusts, grease, oil and moisture and assures the required surface rugosity so that the sprayed material satisfactorily anchors to the substrate.

The use of a pre-heating step immediately before coating deposition helps to eliminate grease, oil and humidity retained on the steel surface by burning and/or volatilization and also favors internal stress elimination and therefore the layer adhesion and cohesion. There is, however, an ideal substrate pre-heating temperature, to be determined for each deposited material. If the substrate temperature is too high, it may burn the polymer, producing gases inside the coating and increasing porosity.

Therefore, according to Rajamäki (2000), during thermal spray, porosity may be, to some extent, controlled with substrate pre-heating temperature. The presence of aluminum particles, such as in composites, may also help decreasing polymer degradation, and consequently, porosity, which can be directly measured using ultrasound (Cudel et al., 2000)

This paper reports an exploratory study into various polymer deposition processes and evaluates their influence on the quality of the produced coating, concerning dispersion, cohesiveness and adhesion onto steel substrates. Different content polymer/aluminum composites and processing parameters were studied as an attempt to identify the most promising process regarding their future application to produce coatings for the oil industry.

METHODOLOGY

Three mixtures of aluminum and medium density polyethylene (MDPE) powder with different weight fractions were prepared, namely, 30%Al/70%MDPE, 50% each and 70%Al/30%MDPE. The powders were all mixed in a "y" shaped mixer. Table 1 shows some properties of the used polymer as given by the supplier.

In spite of the polyolefin advantages such as easy processing, low price, low weight and low water absorption, difficulties still exist. The low flowability of polymer particles during spray may be a problem, which can be controlled by adding products that change the powder flow (Rajamäki et al., 2000). The chemical inertia of these polymers leads to poor interaction with materials such as glass, metals and the majority of polymers. For polyethylene, however, these difficulties can be overcome by its chemical modification, via chemical reactions that modify the molecular structure of the polymer and, as a consequence, its properties.

Thus, the 30%Al/70%MDPE mixture was also prepared with a chemical agent called maleic anhydride (MAN) in order to modify the polymer chemical structure. The grafitization reaction between the polyethylene and maleic anhydride used in this work consists of an addition reaction of succinic groups to the polyolefin, to improve adhesion in the particle/matrix interface and coating material/substrate. The MAN powder was added to the mixtures at different contents (0.5%, 1%, 2% and 3% w/w of MDPE). Another attempt used a previously prepared hot acetone MAN solution (1% w/w of polymer) for a better homogeneity of the reactant to the mixture. This solution was incorporated to the powder mixture, which was then placed in an oven until solvent volatilization yielding a MAN included powder.

Table 1. Polyethylene properties

Melting flow index (2.16kg/190°C)	ASTM D 1238	4.2 g/10min
Density	ASTM D 792	0.935 g/cm^3
Flexure modulus	ASTM D 747	450 MPa
Izod impact strength	ASTM D 256	160 J/m
Softening point Vicat	ASTM D 1525	116°C

Material Characterization

A preliminary characterization of the produced material was carried out via mechanical testing as a first selection for promising mixtures for the deposition process.

Composites of Al/MDPE mixtures were prepared in an injection-molding machine, at 180°C – 200°C depending on the composition. The samples were prepared according to standard tensile strength polymer testing (ASTM D638), from where tensile strength, Young modulus and ductility of the materials were obtained.

Surface Preparation

Prior to all deposition processes, the surfaces were prepared by abrasive blasting with aluminum oxide (Al_2O_3), to improve surface cleaning and mechanical anchorage of the coating material to the substrate.

Thermal Spray Deposition

The thermal spray process used was the flame deposition process, with nitrogen as the carrier gas, in order to minimize polymer degradation. A Rototec gun with feedstock by gravity was used for all Al/MDPE mixtures.

Films were also prepared by pressing grounded injected mixtures on the substrate and consolidating them in place with the aid of a spray gun for comparison with the original thermal spray process.

Hot Pressing Deposition

Al/MDPE powder mixtures and their grounded injected composites were used to coat previously prepared steel surfaces by hot pressing.

Each mixture was uniformly distributed on the surface of a substrate and subjected to heat (200°C) and pressure (approximately 1 MPa) to obtain the different coatings.

Coating Evaluation

Coating/substrate adhesion evaluation was carried out by ASTM C633-79 tensile tests. For that, the mixture was deposited on standard cylinders (25.4 mm diameter), which were then tested in a universal testing machine, as shown in Figure 1. This quantitative test measures the necessary force to debond the coating (Bull, 1991; Bellido-González et al., 1995).

During testing, problems were found regarding failing of the adhesive/coating interface instead of the coating/substrate. When that occurred, the sample was discarded.

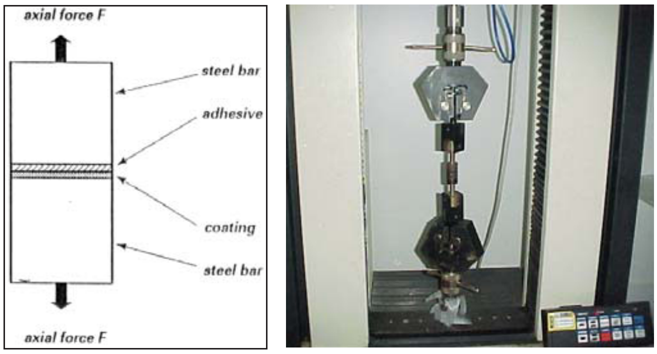

Figure 1. ASTM C633-79 tensile test: (a) Schematic drawing, and (b) Actual test

In addition, the produced coatings were also tested by the qualitative bend test (Fig. 2). This a practical, common use test which allows a visual assessment of the quality of the coating by the observation of coating delamination and cracks or micro-cracks on the bend surface.

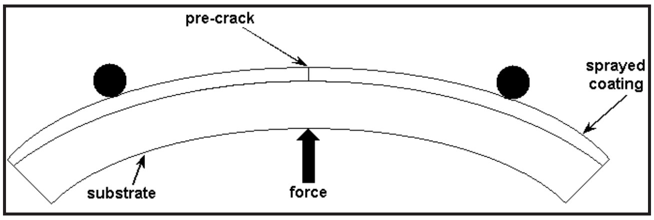

Figure 2. Schematic drawing of the bend test

The morphology of the coatings was evaluated by optical microscopy. For that, coated surfaces after the bend test were cut perpendicularly to the bend line to allow cross-section evaluation.

RESULTS

Material Characterization

Typical curves for the tensile tests of injected composites are shown in Figure 3. Even though the best injection conditions were not yet achieved, the aluminum particles were able to reinforce the original polymer and the obtained composite strength was slightly higher than that of the pure polymer. Besides, the addition of aluminum significantly reduces the materials toughness and this brittle behavior was attributed to the poor adhesion in the aluminum/polyethylene interface.

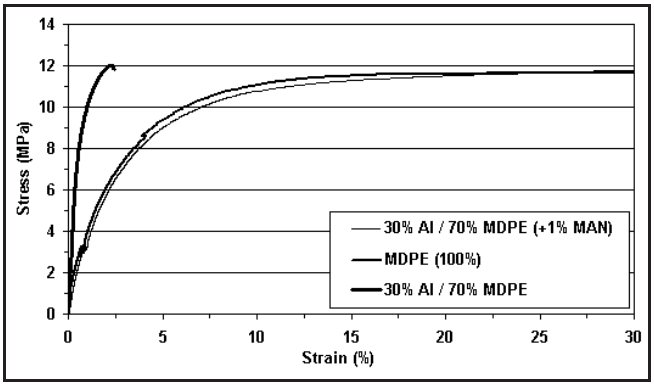

Figure 3. Stress strain curve for the MDPE, unmodified and modified composites (30% Al/70% MDPE)

Furthermore, the presence of the MAN in the composite was responsible for the recovering of the original MDPE ductility, with a small increase of strength and rigidity (Table 2). In fact, the maximum capacity of the extensometer (25 mm) used to measure strain was achieved without fracture. This occurs because the succinic groups grafted to polyethylene compatibilize the aluminum particles to the matrix, improving interface adhesion and hence, composite toughness. This is a promising result, indicating that the mechanical properties of the coating material, such as its cohesiveness, can be tailor-made to suit the application once optimal preparation conditions are established.

Table 2. Mechanical properties of the original MDPE and its mixture with aluminum

	Tensile Strength (MPa)	Young Modulus (GPa)
MDPE (100%)	11.8	0.42
30% Al/70% MDPE	12.5	2.06
30% Al/70% MDPE (+ 1%MAN)	12.0	0.61

Although the 50% aluminum content mixture could be injected, it was not able to provide reproducible results with the used methodology and therefore these composites could not be evaluated. The injection molding equipment used was also not able to prepare composites with 70% of aluminum content due to the low flowability of the mixture.

To estimate the MDPE behavior when deposited by thermal spray, the morphology of the higher aluminum content mixture was studied. For that, the mixture was compacted and heated in an oven (200°C). The obtained mixture was homogeneous (Fig. 4) and with low porosity (Anjos et al., 2002).

Thermal Spray Deposition

During the thermal spray process various difficulties were found. The mixture retained moisture, which agglomerated the powder particles, compromising powder flowability and preventing the mixture from reaching the nozzle of the gun. This problem could be overcome by drying the mixture in an oven at 80°C for 8 hours prior to use.

Figure 4. 70%Al/30% MDPE mixture after simultaneous compacting and heating at 200°C

Another difficulty was that the polymer, when passing through the spray gun's nozzle, severely degraded and stuck to the gun, obstructing the flow of the mixture, due to its low degradation temperature. Thus, it was not possible to deposit high MDPE content coatings with this technique using a conventional gun. Other polymers, with degradation temperatures higher than that of the MDPE are supposed to show better results with this technique.

The use of a spray gun in which the powder feed system does not pass through the flame but after the nozzle of the gun could be able to avoid flow obstruction. This alternative was tried with a Rototec gun, but even with the mixtures well dried, the powder flowability was, again, insufficient to improve material deposition. The polymer also agglomerates within the powder feeding system for the thermal spray and HVOF process due to the high carrier gas (nitrogen or argon) pressure.

Both MDPE granulometries tried (180 μm and 400 μm) showed poor flowability and a possible explanation for this inconvenience relies on the irregular shape of the MDPE powder. The non-spherical particle shape makes it more difficult for the particles to past slip each other preventing the flow.

The difficulties found for the flame spray process were only overcome for the higher aluminum content (70%) and with newer gun models.

Hot Pressing Deposition

Regarding the use of hot pressing for deposition, the 70%Al content coating could not be formed due to the low polymer content which compromised film continuity and cohesiveness. However, the other mistures were able to develop a protection film, which may be important for protective coating against corrosion.

Another attractive noticed characteristic was the smooth surface of the coating. The low friction coefficient of the coating surface may be very useful, once it may reduce turbulence in oil transportation, what reduces corrosion and erosion.

Coating Evaluation

Figure 5 shows the adhesion evaluation for the 30%/70% MDPE mixture. As this figure illustrates, the use of MAN did not improve adhesion for the mixtures applied by hot pressing. However, when the modified composite, previously prepared via reactive injection, was applied, a significant enhancement on adhesion was achieved. In fact, the adhesion value reported in the literature (Rajamäki et al., 2000) is 3.9 to 5.5 MPa for polyethylene, and therefore the mixture with aluminum proves to significantly increase adhesion.

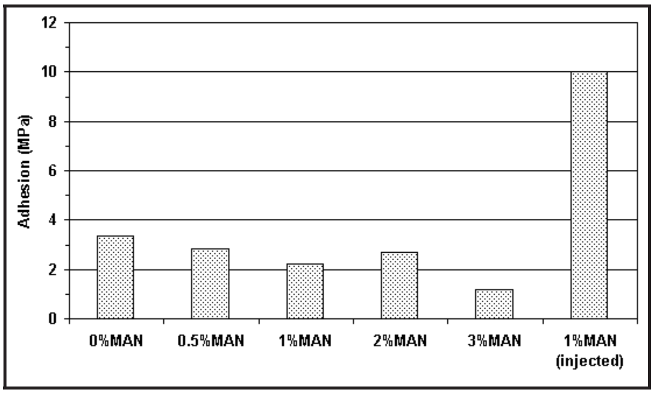

Figure 5. Adhesion of 30% Al and 70% MDPE composite coatings to steel substrate

The bend test also showed promising results even for this very aggressive test which causes high shear stress on the coating layer. Figure 6 shows coatings deposited by hot press for different mixtures, where none of them [30%Al, 30%Al (+1%MAN), 30%Al (+1%MAN) injected and 50%Al] showed surface debonding. Coating cohesion was maintained and no surface cracks or micro-cracks could be noticed.

Some coatings with 50% Al and all the 70% Al ones showed cracks and debonding due to poor phase distribution and lower polymer content, which is ultimately responsible for film cohesiveness.

The behavior of flame aided deposited coatings is shown in Figure 7. The lower aluminum content coating showed good adhesion, cohesiveness and film integrity. However when the thickness of the coating was too high, the coating did not resist the bend test (Figure 7b). The coatings with 50% and 70% aluminum could not also withstand bending, showing the presence of pores and cracks (Figures 7c and 7d).

These coatings, especially those with high aluminum content, also showed a higher roughness when compared to the ones of figure 6.

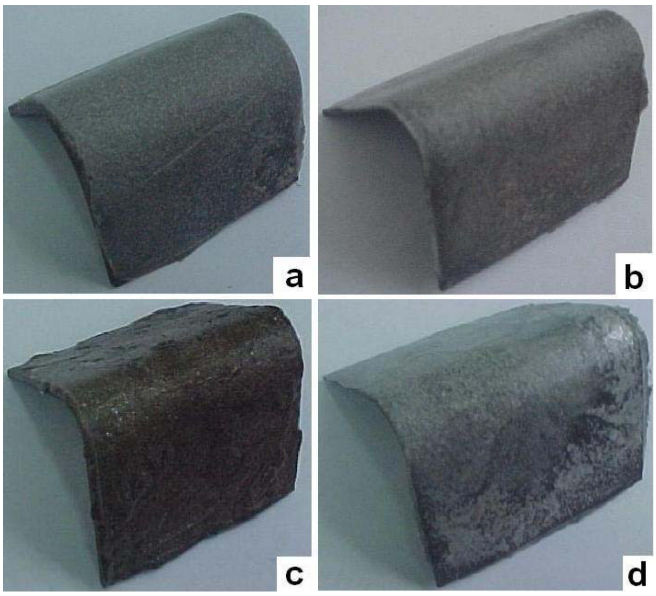

Figure 6. Macro photographs of the hot pressed coatings after bend testing: a) 30%Al; b) 30%Al (+1%MAN); c) 30%Al (+1%MAN) injected; and d) 50%Al

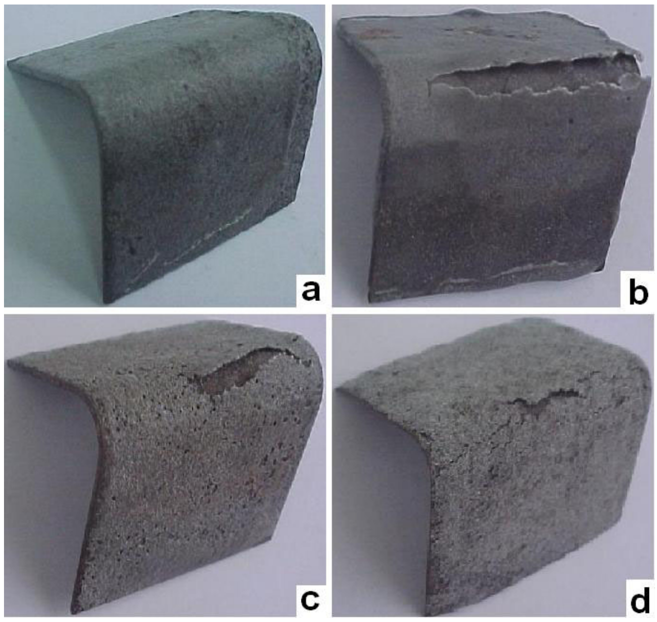

Figure 7. Macro photographs of the flame aided deposited coatings after bend testing: a) 30%Al; b) 30%Al (higher thickness); c) 50%Al; d) 70%Al;

In figure 8, bent surfaces of figure 6 were evaluated under an optical microscope. One can notice the lack of microcracks and that adhesion in the coating/substrate interface is adequate even though this is the point of maximum shear stress. Whatever the deposition process, the use of MAN have shown to be able to produce thick (600 μm) stable coating layers in opposite to those without MAN which only achieved around 300 μm.

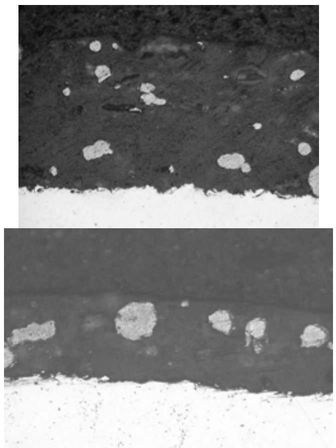

Figure 8. Optical microscopy photographs of the 30%Al – 1%MAN hot pressed composite (a) and 30%Al flame aided deposited coatings (b)

CONCLUSIONS

This paper reports an exploratory study into various polymer deposition processes. Different content aluminum/polymer composites and their performance as coatings were investigated.

The results showed that the use of aluminum/MDPE for coating applications is a promising alternative for corrosion protection problems. The low friction coefficient surfaces obtained and the adequate adhesion of the films to steel substrates demonstrate the potential of these coatings for their use in the oil industry.

The use of MAN (maleic anhydride) in the composite was crucial, being responsible for the MDPE to recover its ductility, with a small increase of strength and rigidity, as well as a significant enhancement of coating adhesion to substrate.

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