About Coatings and Cathodic Protection: Electrochemical Features of Coatings Used on Pipelines

Isabel C.P. Margarit,† Oscar R. Mattos, and José Roberto R.M. Ferreira—Federal University of Rio de Janeiro*
Joaquim P. Quintela—Petrobas, Petroleo Brasileiro S.A.

The behavior of a coal tar, a polyethylene, and a fusion bonded epoxy was evaluated. Coated samples with and without intentional failures exposing the metallic substrate were submitted to different levels of cathodic polarization. The process of delamination was monitored with current and impedance measurements. The delamination was quantified by a standard method. No quantitative relationship between the delaminated areas and electrochemical parameters could be found; the reasons are discussed in terms of the properties of the coatings. It was shown that the higher the dielectric strength of coatings, the more critical the role of pores and mechanical damage in determining cathodic protection effectiveness.

INTRODUCTION

Nondestructive methods for monitoring defects in organic coatings are economically attractive. In the plant, the differences between on-off potentials and the Pearson Method[1] have been used. More recent research highlights noise measurements[2] and impedance spectroscopy[3-6] as other possibilities. In the case of impedance spectroscopy, it was shown that detailed knowledge of the aging process of the coating is essential for correct data interpretation.[7-8] There is a regrettable lack of detailed information on the aging of real coating systems. The present work deals with three of the most common coatings used on pipelines: coal tar (CT), polyethylene (PE), and fusion bonded epoxy (FBE). Some delamination problems have been reported for PE and FBE used simultaneously with cathodic protection.[9] The main purpose of this study was to monitor with electrochemical techniques the delamination process of samples coated with PE, FBE, and CT submitted to different levels of cathodic polarization. Based on these results, this paper discusses the effectiveness of cathodic protection on delaminated areas and the use of electrochemical methods for monitoring the integrity of these kinds of coatings.

EXPERIMENTAL

Materials

The coatings consisted of: (1) a fusion bonded epoxy (FBE) applied in one layer on blasted steel; (2) a low density polyethylene (PE) applied by lateral extrusion in three layers: the first layer is a powder epoxy primer, the second and third layers are the PE itself; and (3) a coal tar (CT). The area of the working electrodes was 80 cm^2. The total dry coating thickness was 500 μm for the FBE and 3 mm for PE and CT. Free films obtained by promoting cathodic disbondment from the steel substrate were also used. The working electrolyte was NaCl 1% + Na_2CO_3 1% + Na_2SO_4 1% as recommended by ASTM G8[10] for cathodic delamination tests. Samples with and without intentional failure were tested. The failure consisted of holes drilled through the coatings until the metal was exposed. The area of the failures was 0.36 cm^2 for FBE and 1.4 cm^2 for CT and PE. These areas were established in accordance with the thickness of the coatings following the ASTM G8 recommended practice.

Testing Conditions

The different samples were tested under several polarization levels at ambient temperature. The samples with intentional failure were polarized at –0.85 Vsce, –1.0 Vsce, –1.2 Vsce, and –1.5 Vsce. This last potential corresponds to the upper limit recommended by ASTM G8. The samples without intentional failure were polar-

*EE/COPPE/PEMM, P.O. Box 68505, 21945-970 Rio de Janeiro, Brasil; email: omattos@metalmat.ufrj.br; Cidade Universitária, Rio de Janeiro.
†EQ/DPI/COPPE; email: margarit@metalmat.ufrj.br

ized at –1.2 Vsce and –5.0 Vsce. The –5.0 Vsce is far beyond the cathodic potentials applied in practice, but it was necessary to accelerate the aging of the samples without intentional failure. In a previous study, it was verified that this potential, although very high, accelerates but does not change the mechanism of the aging process of various coatings.[11]

Cathodic Disbondment

The cathodic delamination of FBE, PE, and CT samples without failures was measured by stripping the coating from the borders of a square-cut after 90 days, 210 days, and two years of polarization at each potential. The delamination of samples with intentional failure was measured after 90 days by stripping the coating from the borders of the original hole. The results of the measurements are shown as the ratio of the delamination area to the original intentional failure area (S = final area/initial area).

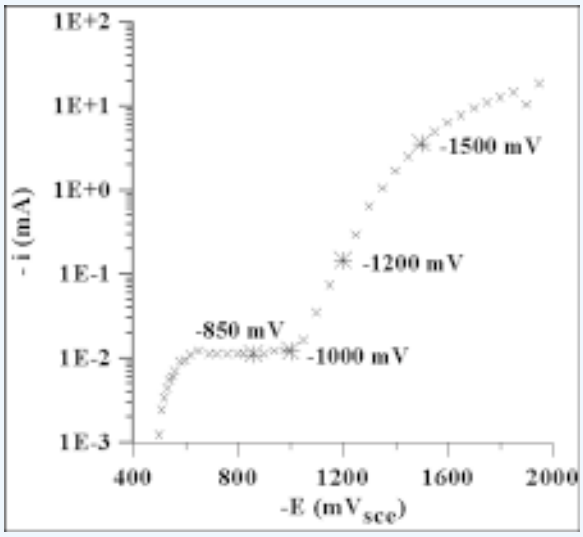

Figure 1—Cathodic polarization curve of the substrate on the working electrolyte.

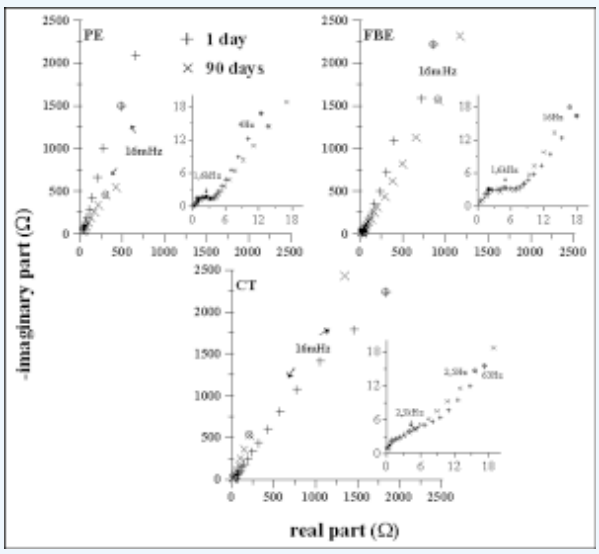

Figure 2—Impedances of FBE, PE, and CT at –0.85 Vsce. Samples with failure.

Polarization Curve

A cathodic polarization curve was obtained for the steel substrate on the working electrolyte. A steady-state curve was performed under natural convection with an Omnimetra Model PG-05 potentiostat/galvanostat.

Electrochemical Monitoring

The cathodic current flowing for each sample and the changes of the electrochemical impedance were monitored with testing time. The impedance measurements were performed under potentiostatic control at the respective polarization potentials. The instruments consisted of an Omnimetra Potentiostat Model PG09 and an FTA Solartron 1250. All measurements were done in a grounded Faraday cage.

RESULTS AND DISCUSSION

Samples with Intentional Failure

The four potentials used in the cathodic delamination tests were selected based in the cathodic polarization curve of the steel substrate shown in *Figure* 1. Two of them, –0.85 and –1.0 Vsce, correspond to the oxygen plateau. The other two, –1.2 Vsce and –1.5 Vsce, correspond to the water reduction reaction. Ninety days after the beginning of the tests, the polarizations were interrupted and the delamination was measured for three samples at each potential. The results are presented in *Table* 1. PE was characterized by a continuous increase in the delamination area with the polarization level. On the other hand, the polarization effect on FBE and CT was clearly evidenced only at –1.5 Vsce. Indeed, between –0.85 and –1.2 Vsce, it was possible to find samples of these last two coatings with similar delaminations, though this was more evident for CT. It should also be noted that until –

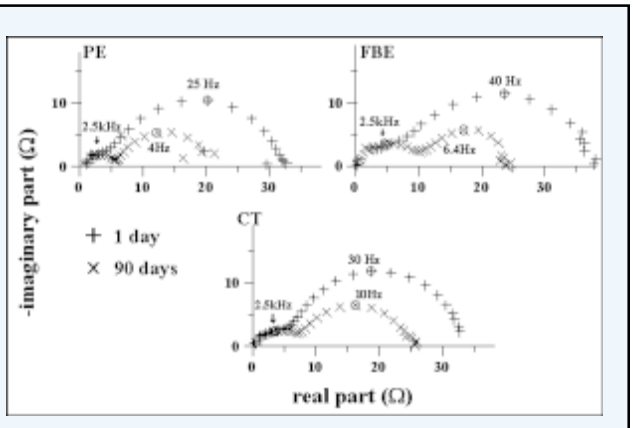

Figure 3—Impedances of FBE, PE, and CT at –1.5 Vsce. Samples with failure.

1.2 Vsce, there was no clear evidence that either PE or FBE provided better performance than CT, the most traditional coating used on pipelines. It is important to emphasize that this last comment is restricted to the present study. The relative delamination of the coatings may change with other surface treatments, but this is out of the scope of the present discussion.

The behavior of these samples was monitored with impedance and current measurements, but only the results at the extreme conditions, –0.85 Vsce and –1.5 Vsce, are discussed. The impedance diagrams concerning –0.85 Vsce are given in *Figure* 2 for one and 90 days. The diagrams are characterized by a small capacitive loop at high frequencies followed by another larger one. The loops at high frequencies are shown with expanded scale on the same figure. Capacitance values for the first loop are around 10^{-5}F on the first day and stay practically constant for 90 days, despite the increase in the delaminated area presented in *Table* 1. The loop at these frequencies is restricted to the area of direct exposure of the metal to the electrolyte. Indeed, it can be seen that the increase in the area resulting from cathodic delamination is reflected only at lower frequencies in the diagrams. This is more evident at –1.5 Vsce, as shown by the diagrams in *Figure* 3. At this potential, the second capacitive loop has its limit well defined at lower frequencies, because the main cathodic reaction changes from oxygen to water reduction. At this polarization level, it is clear that Rp (polarization resistance) values are reduced with time due to the increase of the delaminated area around the failure. This kind of behavior has already been commented on by Hirayama et al.[12] who modified the breakpoint frequency method.[13] Indeed, the authors' idea was to use parameters in the high frequency range to detect delamination problems in coatings. However, in the presence of failures with metal exposure, the authors proposed to use a parameter at low frequency range.

Current-time curves for the three samples of FBE, PE, and CT at –0.85 Vsce and –1.5 Vsce are shown in *Figure* 4. At –0.85 Vsce, it can be observed that after 90 days all samples are characterized by similar or even lower current values than the ones measured on the first day of polarization.

The value of –0.85 Vsce is not high enough to minimize the effect of eventual changes on the free potential during the current-time measurement.[11] In this case, the delaminated area is not very important and the current plots diminish slightly with time. The situation is different at –1.5 Vsce, when a meaningful increment of the currents can be observed. In *Table* 2, the values of the current, Rp and delaminated area are shown for the first and 90th day of the test. From this table, it can be seen that qualitatively the kinetic parameters change coherently with the increase of the delaminated area: Rp diminishes and the current increases. On the other hand, no simple quantitative relationship can be found between these parameters and the areas. The increment in area is only partially contributing to the increase in current or diminishing Rp. It is also possible to observe that the greatest discrepancies occur for the samples with the largest area increments. This aspect has already been observed for another type of coating, and it was explained by heterogeneity on the electric field at the coating/metal interface.[7-8] Indeed, the delaminated area is not homogeneously polarized. Therefore, the increase observed in the area is not totally reflected by the kinetic parameters.

Table 1—Degree of Cathodic Delamination on Three Samples of PE, FBE, and CT at Different Cathodic Polarizations

–0.85V		–1.0V		–1.2V		–1.5V	
Sample	S	Sample	S	Sample	S	Sample	S
PE1	1.5	PE4	2.2	PE7	4.0	PE10	5.3
PE2	1.8	PE5	2.6	PE8	4.0	PE11	5.3
PE3	1.8	PE6	2.6	PE9	4.0	PE12	5.3
FBE1	8.9	FBE4	13.0	FBE7	15.0	FBE10	46.4
FBE2	13.0	FBE5	12.7	FBE8	13.0	FBE11	50.4
FBE3	7.3	FBE6	15.0	FBE9	13.0	FBE12	50.4
CT1	2.4	CT4	1.8	CT7	1.9	CT10	2.5
CT2	2.8	CT5	1.7	CT8	1.7	CT11	9.7
CT3	2.0	CT6	2.2	CT9	1.7	CT12	18.5

$S = \frac{\text{Total area}}{\text{Initial area}}$

Table 2—Variation of Current, Rp, and Delaminated Area of FBE, PE, and CT at –1.5 Vsce

Sample	i_0 (mA)	i_f (mA)	$\frac{i_f}{i_0}$	Rp_0 (Ω)	Rpf (Ω)	$\frac{Rp_0}{Rp_f}$	S
PE10	3.8	7.9	2.1	38	14	2.7	5.3
PE11	5.1	8.1	1.6	32	20	1.6	5.3
PE12	2.4	5.8	2.4	35	22	1.6	5.9
FBE10	2.6	5.1	2.0	36	14	2.6	46
FBE11	2.2	5.9	2.7	43	14	3.1	50
FBE12	3.0	5.2	1.7	31	18	1.7	50
CT10	3.4	5.2	1.5	22	13	1.7	2.5
CT11	4.1	5.4	1.3	24	17	1.4	9.7
CT12	4.1	6.1	1.5	30	16	1.9	18.5

i_0 = current after 1 day; i_f = current after 90 days.
Rp_0 = pol. res. after 1 day; Rp_f = pol. res. after 90 days.

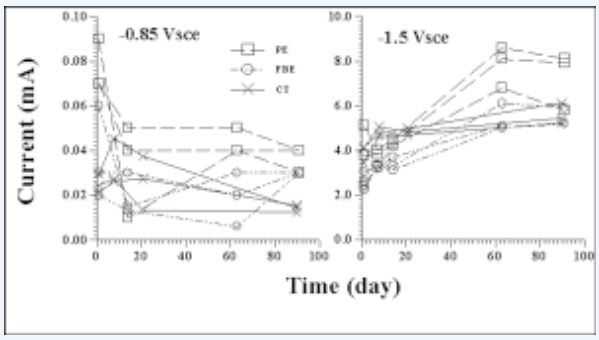

Figure 4—Current-time curves for FBE, PE, and CT at –0.85 Vsce and –1.5 Vsce. Samples with failure.

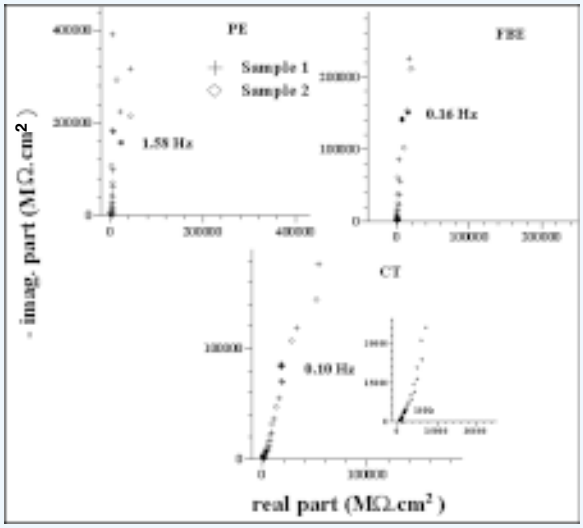

Figure 5—Initial impedances of FBE, PE, and CT. Samples without failure.

Samples Without Failure

The initial impedances for two samples of each coating are shown in *Figure* 5. Vertical straight lines exhibiting behavior similar to quasi-ideal capacitors characterize the diagrams of PE and FBE. The diagrams of CT samples are different, suggesting the existence of a small capacitive loop at high frequency. This behavior may be an indication that diffusion processes are occurring through CT since the first days of contact with an electrolyte.

In *Figure* 6, the current-time curves for two samples of each coating are shown for both potentials. These curves show higher currents flowing through CT. Consistent with this, after 210 days at –5.0 Vsce, only CT exhibited signs of deterioration being completely swamped with the electrolyte. At the same time, PE and FBE did not present any adhesion loss, but after two years under polarization at –5V, these coatings were completely delaminated whereas CT remained partially adhered to the substrate. Although completely delaminated, curiously there was no electrolyte at the interface between PE or FBE and the metal. These delaminated films had

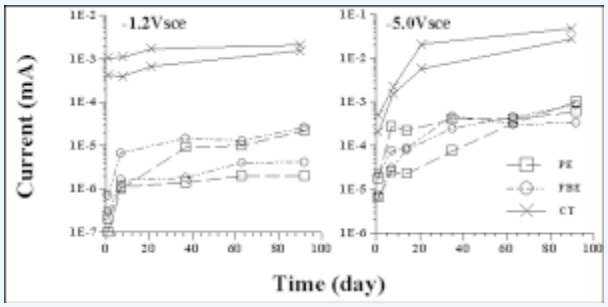

Figure 6—Current-time curves for FBE, PE, and CT at –1.2 Vsce and –5.0 Vsce. Samples without failure.

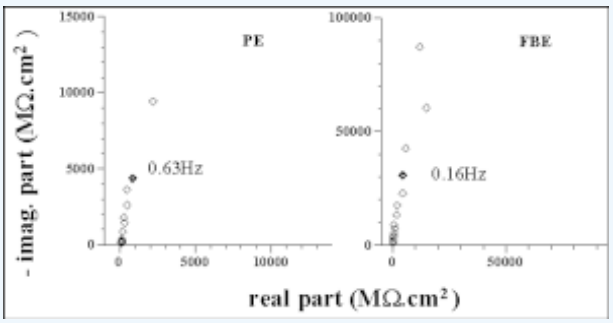

Figure 7—Impedance of FBE and PE after two years at –5.0 Vsce. Measurements with detached films in a four-probe cell.

their impedances measured in a four-probe cell.[7-8] As it can be seen in *Figure* 7, the impedance of PE and FBE free films remained extremely high. Then, from a practical point of view concerning the cathodic protection, if the electrolyte reaches the metal in such condition, via a pore or a mechanical damage always present in a real structure, the cathodic protection will not be assured under these coatings.

The features observed for CT, FBE, and PE justify the differences between current increase and delaminated area. FBE and PE delaminate without penetration of electrolyte; consequently, there is no reason for a proportional current increase. On the other hand, if the electrolyte reaches the metal through a failure, the high impedance of these two coatings will not allow the electric field to act in the occluded delaminated area.[8] In the case of CT, redistribution of the electric field may also occur, but the more important fact is that it swamps and allows current to flow not only through the failure but also through the coating itself. Thus, the risk of absence of cathodic protection is lower for CT. This result is consistent with previous studies[11] which show that the most resistive coatings are not always the best to be used with cathodic protection. The last important point to be outlined is that for all studied cases, there is no reason for a simple relationship between current, Rp or any other electrochemical parameter and delaminated increasing area. Indeed, the delamination process is a function of the coating properties that will define the electric field distribution on these areas. By electrochemical methods, in particular by impedance, the appearance of a defect exposing the metallic substrate can be easily detected, but the extent of delamination that results from this initial failure can not be quantitatively determined.

CONCLUSIONS

Results on three coatings show that delamination is not a simple function of electric field intensity, but that it depends on intrinsic features of the coatings, which will, among other things, determine the electric field distribution at the metal surface. In consequence, no quantitative relationship between the delaminated area and the electrochemical parameters could be established for the com-

mercial coatings studied here. The characterization of the cathodic polarization effects on the three coatings, complemented by electrochemical measurements, corroborates that the presence of failures on FBE and PE can be more critical than on CT. The higher dielectric strength of FBE and PE impedes the action and complicates the monitoring of cathodic protection on defective areas.

ACKNOWLEDGMENTS

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