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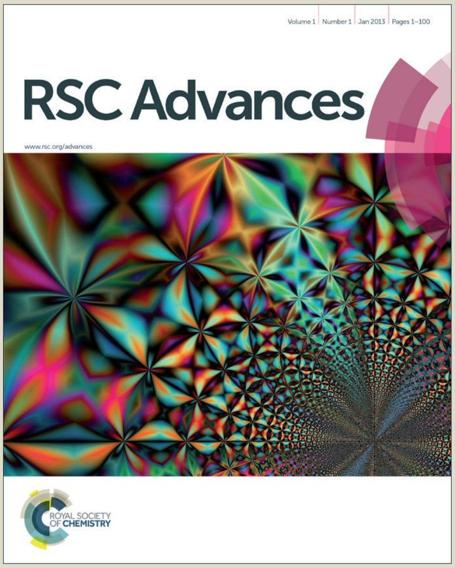

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Spent tyres valorisation: new Polymer Modified Asphalts for steel protection under a marine aggressive environment

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Waste valorisation is a topic in the limelight since environmental concerns are furthering a better use of raw materials. Annually, millions of tons of waste tyres are generated worldwide and represent a great environmental threat that could be used in the development of novel materials for effective protection against steel corrosion. In this work, the performance of 8 new Polymer Modified Asphalts (PMA)-based coatings made up from spent tyres was evaluated on steel samples. Accelerated tests (salt spray, humidity and accelerated aging) as well as adherence and impact studies at laboratory scale were carried out prior to two year-exposure investigation under a very high aggressive marine zone. The analysis of the results revealed the suitability of most of the PMA compositions in terms of anticorrosive protection, adherence and impact resistance. The suitability of these PMA compositions was validated by applying them in automobiles submitted to an aggressive marine environment.

Keywords: Polymer modified asphalts, protective properties, marine environment, spent tyre valorisation, laboratory and field tests

Introduction

Waste valorisation is a topic of a great scientific interest for many researchers in different disciplines.[1-3]Every year, around 4.4 million tons of waste tyres in the world are discarded, which represents a great environmental threat. The presence of natural and synthetic rubbers in tyres accounts for approximately 60%, which makes this waste a potential raw material for a diversity of applications.[4,5] Therefore, the search of technically, economically and environmentally advantageous solutions is of paramount importance. Retreading, recycling and energy recovery are the three main treatments employed for tyres valorisation. With regard to recycling, several investigations have been focused on the development of rubber modified bitumen where rubber particles act like modifying agents improving the bitumen properties.[6,7] This type of materials is also known as composites and they are composed by a matrix and a filler material which reinforces the former.[8,9] This is an environmentally sustainable alternative in line with the current European Union policies (Directive 2000/53/EC), which states that at least 85% of end of life vehicles weight must be re-used or recycled by the present year 2015.[10]

Bitumen and bituminous binders are widely employed for roofing and road pavements because of their interesting adhesive and load resistance properties.[11]

However, there are some pavements defects, such as rutting at high temperatures, crack initiation and propagation in the low temperature region and low elastic and viscous properties at high in-service temperature, that favour permanent deterioration, thus reducing their durability.[12,13] These distresses can be overcome with the addition of ground tyre rubber, which improves their mechanical properties.[7,13] Also, combinations of bitumen modifiers have been proposed to improve mechanical and rheological properties, namely rubber and recycled polyethylene,[14] crumb rubber and a set of special additives,[15] organic layered silicates[16] and expanded vermiculite.[17]

The applicability in roofing, waterproofing, and sealing industries as well as the development of novel asphaltic modified emulsions have been patented.[18,19] More specifically, rubber modified asphalt applied by spraying allows forming a stable and tough waterproof layer over the surface, as already demonstrated for buildings and structures protection against moisture and rust.[19] Recently, a new asphalt material constituted by a polymer and a polyol was developed and it turned out to confer remarkable waterproofing properties and protection from physical damage.[20]

In general, the aforementioned studies have concentrated their efforts in evaluating the rheological and mechanical properties of different modified bitumen compositions for

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pavement or roofing applications. However, only few investigations have referred to their anticorrosive properties and their application as waterproofing and rust proofing. Hence, these limitations have motivated the development of new compositions of rubber modified asphalt (PMA) at laboratory scale. In this work, the protective properties of 8 new compositions were assessed trough accelerated and outdoor exposure tests (aggressive marine environment), as well as the adherence and impact resistance. Also, their waterproofing and sealant properties were also evaluated, together with their anticorrosive capacity, as a prior step to their application in transport equipment such as bodyworks.

Materials and methods

Materials

Samples of low carbon steel (SAE-AISI 1010), with dimensions (150 mm x 100 mm x 1 mm) and chemical composition indicated in Table 1, were employed for classifying the corrosive aggressiveness of the specific area under study. The surface cleaning consisted of a degreasing with commercial grade naphtha and furthering an immersion for 3-5 min in wt.% hydrochloric acid solution (1:1 in distilled water), followed by a thorough rinsing with distilled water. Then, samples were dried and kept in a desiccator with anhydrous $CaCl_2$ for at least 24 h. Finally, they were weighed and kept again in a desiccator till the beginning of the experiments, one part for corrosion study and the other one as a substrate of PMAs coatings.

Insert Table 1

Rubber modified asphalt compositions

After preliminary investigations where several experimental designs were carried out and optimized, 8 new compositions were carried out to be used in the present work, following a patented procedure.[21] Briefly, they are composed of a matrix (oxidized asphalt) and a reinforcement (powder particles of recycled tyre rubber with 0.21 mm of diameter (US mesh 70) joined trough a binding agent). The rubber is a generic term that can describe elastomeric materials. The binding agent are insoluble soaps obtained from the saponification of soluble soaps (waste material) coming from aliphatic acids derivatives, from glycerides and waxes.[21]

The obtained PMAs are semisolids at room temperature and with a high softening point. The percentage of polymer (rubber) and the softening point in each composition is presented in Table 2. More details about the PMA composition are offered in a patent that is under submission. These data were obtained from the average of at least three measurements for each composition.

Insert Table 2

A uniform film over the substrate was carried out by applying the 8 melted PMAs with a spatula. Degradation of the polymers was observed at temperatures higher than 130ºC. Once the product was hardened, samples were packed and kept in a desiccator till the beginning of the experiments.

Four steel specimens coated with the PMAs compositions were prepared (for each variant), three for the field study and the forth (kept in a desiccator) as a blank for visual comparisons. More samples were also prepared for laboratory tests. Replicates were always included in order to ease the achievement of statistically significant conclusions.

Laboratory tests

Laboratory test were based on different normalized assessments such as adherence and impact test as well as accelerated ones, which together with outdoor exposure results allows getting the main objective of the present investigation. Three replicates for each composition and each test were prepared and the data achieved were obtained from the average of three values.

Accelerated tests

Salt spray test was performed in a climatic chamber, model Q-FOG C.C.T. where steel samples covered with PMAs were exposed. The required conditions for the test were the use of sodium chloride solution (50 g/L +/- 5 g/L) with a density at 25ºC between 1.0255 and 1.0400 g/dm^3, pH: 6,5 - 7,2 and temperature 35 +/- 2°C, in agreement with the UNE-EN ISO standard 9227.[22] The demands for samples assessment were 1000 hours (10 cycles of 100 hours each) in the chamber without the appearance of typical failures such as blistering, cracking, rusting and sensitive delamination, in accordance with the UNE-EN ISO standard 4628.[23] Before evaluation, coated specimens were rinsed with water (after each cycle) to remove the rests of salts on the surface.

Humidity test was carried out in a humidity cabinet, model CCM/0/300, where the conditions of the assay were 40 +/- 2ºC and 100% of relative humidity with constant condensation over the steel specimens (covered with PMAs), according to the DIN EN ISO standard 62700.[24] The requirements for samples evaluation were the same as those mentioned for salt spray test.

The accelerated aging test was conducted in the QUV chamber (model QUV/SE) in accordance with ASTM D standard 4799.[25] Coated specimens were submitted to alternated cycles of radiation and humidity for 1000 hours. Fluorescent lamps were employed for UV-A radiation at a wavelength of 340 nm and temperature between 60-80 ºC (radiation cycle), followed by condensation at 50ºC (humidity cycle). Samples evaluation was performed at the end of every cycle (100 hours each). The absence of significant physical damages in relation to the reference samples for 1000 hours was targeted.

Adherence test

Adherence test was performed following the pull-off method, as stated in the UNE-EN ISO standard 4624.[26] Measurements were performed by using and adhesion tester model ERSAD.

Impact test

The procedure described in the ASTM D2794 standard was followed[27]for the impact resistance test on bitumen modified panels. The test was done for a sphere of 0.9 Kg of weight and 15.9 mm of diameter and at three different heights (25, 50 and 100 cm). An impactometer (model 03040 10) was used for impact measurements.

Adherence and impact tests were performed over steel samples covered with PMA at initial time.

Outdoor exposure testing

Both steel and PMAs samples were submitted to outdoor exposure test at the testing station located at Playa Caleta hotel, as can be seen in Fig. 1.

Insert Fig. 1

It is located in Varadero city (Matanzas, Cuba) 250 m far from the north coast. The latitude and longitude is 23º 9' 13" N and 81º 15' 5" W, respectively. This place is a marine area and fulfils the general requirements for this type of experiments. Specimens (steel and PMA coated steel) were exposed in a rack, facing south, and at 45º to the horizontal, following the recommendations of the ISO 8565 standard.[28] Three steel samples (for corrosion rate determination at each exposure time) and three PMA specimens applied on steel substrates (for each PMA variant) were tested.

Determination of corrosive aggressiveness

Steel samples subjected to outdoor conditions for 24 months were picked up (at scheduled times) and cleaned in a specific solution (500 ml HCl, 500 ml distilled water and 3.5 g hexamethylenetetramine) until complete elimination of corrosion products.[29] Subsequently, the specimens were rinsed, dried, packed and kept in a desiccator during 24 hours. Then, they were weighed with a weighing accuracy of ±1 mg and the weight loss obtained (average of three samples) was used to determine the corrosion rate, according to the demands of the ISO standard 9226.[30] The classification of corrosivity was carried out by means of the average of the annual corrosion rates, conforming to the ISO standard 9223.[31]

Evaluation of PMAs degradation

The 8 PMAs applied over the steel panels were subjected to outdoor exposure test for 24 months. The failures evaluation of the PMAs composition was carried out following an specific scheduled time in agreement with the UNE-EN ISO standard 4628[23] and was ended when important defects were observed. Typical defects such as blistering, rusting, cracking and flaking were assessed with time by visual comparison between the samples studied and standard photographs specifically designed for each failure.[23] This test gives us quantitative information about coatings deterioration with time such as the quantity and size, as well as the intensity of blisters, cracks and flakes. In the case of rusting failure, the percentage of rusted area can be estimated. Results presented are the average of three tested coated panels for each PMA composition at each exposure time.

PMAs applications in transport equipment

The most promising PMAs compositions were applied in transport equipment such as cars bodyworks, under "high" (category C4) and "very high" (category C5) aggressive atmospheres for two years. The coating assessment was performed by visual inspection (once a year) with the aim to detect possible failures, following the UNE-EN ISO standard 4628.[23] Digital photography was also employed.

Results and discussion

Evaluation of PMAs performance submitted to laboratory tests

First of all, an adequate compatibility of PMAs with the substrate was confirmed after the salt spray test. After approximately 450 hours of exposure some surface softening was observed, which led to a slight release of rubber particles from the coating that is not directly adhered to the metallic base. This phenomenon is more evident in this assay than in the humidity one, probably due to the rinsing of samples with water after each cycle to remove the rests of salts on the surface. As can be noticed in Fig. 2, the 8 PMAs specimens under study showed no rusting (metallic substrate) for 1000 hours in a salt fog chamber. Just some degree of oxidation was detected in the borders since they had not been protected in order to ease samples mounting inside the chamber.

Insert Fig. 2

An apparent superficial detachment of the material was detected after 400-500 hours of testing in the humidity test cabinet. This was more evident in the salt spray test. From 700 hours on (7 cycles), a hardening of the material was recorded indicating a slightly superficial flexibility lost, which led to a slight cracking of the film surface at the end of the experiment. Then, after 1000 hours (10 cycles) and 24 hours more outside the humidity chamber, it can be stated that the proposed coatings fulfil the requirements of the standard.

Even though some hardening and loss of flexibility occurred after seven cycles in the QUV chamber, the suitable performance of the PMA compositions was demonstrated after 1000 hours under standard ultraviolet radiation and temperature conditions. Therefore, the coatings also passed the present assay, in agreement with the demands established in the standard.

As observed during the accelerated tests, a slight release of rubber particles from the coating was demonstrated in the PMAs composition. This phenomenon was more evident in those compositions with higher content of rubber particles (PMA 2 > PMA 8 > PMA 3, etc).

The increase of rubber content in PMA contributes to promote a lower adherence, so a higher content of this material should be evaluated. An adherence test was carried out for the composition 2 with the highest relative rubber content. After the assessment, very low cracking and contraction because of flexibility loss was checked, so a scarce release of material due to the rupture of the external layers was detected. The rupture occurred at 225 psi (1.5 MPa), and 100 psi (0.67 MPa) is the maximum stress in agreement with the pull off standard.[26] Results confirm that, even though a pressure higher than the maximum limit (more than doubled) was used, the observed damage is just superficial. Hence, an adequate adherence of the composition 2 to the steel substrate was demonstrated. Consequently, compositions with lower rubber content will pass the tests successfully and less release of material is expected to occur. The latter is supported by the greater relative content of oxidized asphalt and binding agent, thus leading to a higher adherence. This performance, in addition to its flexibility and easiness to be applied with spatula (in hot) widen its application in the joins: metal-metal, metal-mortar, metal concrete and asbestos-cement.

The adherence test results suggest that lower rubber content will lead to a higher adherence in the PMA compositions. These compositions are more adequate to be applied in a liquid form by spray, because a greater rubber content could block the product output for spray applications.

On the other hand, the higher rubber content in PMAs compositions, the greater the impact resistance. This is closely related to the flexibility of the PMA due to the polymer presence. Hence, a high rubber content composition was evaluated (PMA 8). The results of the impact test at three different heights (25, 50 and 100 cm) are summarized in Table 3.

Insert Table 3

As can be seen, the sample tested presents a high endurance to the applied load (0.9 Kg) at 25 and 50 cm of height, and no release of the coating is observed. However, a complete detachment of the coating at 100 cm of height is observed, probably due to the higher rubber quantity in the composition which originated a diminution of the coating adherence to the steel base. Although the samples tested at 100 cm of height failed, the results obtained for 25 and 50 cm of height are considered positive, bearing in mind that the material will not be exposed to such extreme conditions (0.9 Kg of weight and 100 cm of height). Hence, the results confirmed the appropriateness of the coatings, as demanded by the standard.[26]

Assessment of PMAs deterioration exposed to outdoor conditions

Before the evaluation of the PMAs deterioration in outdoor conditions, the determination of the corrosive aggressiveness of the selected area was carried out. Following the classification system for the corrosivity of atmospheres established by ISO standard 9223,[31] and once the annual average of the corrosion rate (CR) of the low carbon steel was calculated (671.95 g/m^2), the area under study was concluded to be an environment with "very high" (category C5) corrosive aggressiveness. This experimental stage constitutes a fundamental step which will determine the surface preparation, design problems, protective systems, maintenances, etc. The weight loss for 1, 2, 3, 6 and 24 months of outdoor exposure was also determined, which is summarized in Table 4.

Insert Table 4

Monthly weight loss trend for carbon steel can be visualized in Fig. 3, where two differentiated climate periods are clearly recorded. On the one hand, the winter or dry season (November-April) is characterized by a predominance of north-northeast winds, so the marine aerosol concentrations and the mass loss are increased. On the other hand, the summer or rain season (May-October) leads to a reduction of the weight loss due to the weaker effect of the north winds, in agreement with previous studies.[32]

Insert Fig. 3

Afterwards, the evaluation of the macroscopic defects presented on the protective films after 24 months of exposure was performed, following some codes presented in Table 5.[33] These codes are related to specific values aiming at favouring the comparison among defects.

Insert Table 5

A summary of the PMAs defects during experimentation time is shown in Table 6, as obtained from the average of three tested coated panels for each scheduled time.

Insert Table 6

Among the eight compositions tested, only 1 and 4 showed cracking (type 2 S(3))[33] after 3 and 21 months of exposure, respectively. The morphology of the cracks was without a preferential direction.[33]This behaviour is considered acceptable in agreement with the evaluation scale (Table 5), and it can be visualized in Fig. 4. The aforementioned is supported due to the beneficial effect of rubber in the PMAs. The addition of rubber, from recycled automobile tyres, to an asphalt binder, substantially reduces the rate of oxidative hardening of asphalt and increases its useful life.[34]

Insert Fig. 4

This failure is not considered important due to its superficial nature. Also, these PMAs compositions showed neither blistering, nor rusting and flaking after two years of exposure under a very high aggressive location. However, both compositions were discarded due to the cracks detected which can promote the access of water and pollutants trough the layer, thus affecting its anticorrosive protection.

In relation to the rest of the compositions tested, a promising protective performance was concluded after 24 months under very high aggressive environment as can be noticed in Fig. 5.

Insert Fig. 5

This is in compliance with the UNE-EN ISO standard 12944-5[35] referred to the selection of coating systems, since a durability from 2 to 5 years without failures is required.

Evaluation of PMAs applications in the transport technique

From the results obtained, both PMA 2 (with high amount of rubber) and PMA 5 (with the lowest quantity of rubber) were selected to be applied as semisolid coatings. Hence, they were produced at a pilot plant existing in our research group. The composition 2, a semisolid PMA (DISTIN 403), was applied in the metal-metal joins of car fenders for coating the car floor (inside part) as well as for sealing some parts of the body car (Fig. 6). Once applied, an average thickness around 1 and 2 mm was reached. After the yearly visual inspections, the material was demonstrated to act as an anticorrosive and waterproofing coating providing resistance to water and the aggressive media. It was flexible, mouldable and helped to simultaneously reduce the noise produced outside the car.

Insert Fig. 6

The composition 5, a liquid PMA of solvent type (DISTIN 403 L) with a semisolid base was sprayed to the outside part of the car floor. The new coating was able to withstand the impact of water and particles and it also showed an excellent adherence and corrosion resistance, for an average thickness of 138 ± 10 µm. After more than one year of exposure, the PMA applied on automobiles subjected to an aggressive environment confirmed its excellent performance as stone chip coating (Fig. 6), and also provided a reduction of noise derived from impacts of stones with the exterior surface of floors. In summary, as a result of all these tests, two types of PMA with specific characteristics and applications have been identified as follows:

- PMA composition as an anticorrosive coating for the transport equipment.
- PMA composition as a waterproofing and sealant coating for floors.

Conclusions

In this work we have demonstrated the suitability of Polymer Modified Asphalts (PMAs) containing spent tyre-powder to protect steel substrates against corrosion under very high aggressive environments. From the results achieved, a suitable adherence and impact resistant was demonstrated. Accelerated and outdoor exposure tests under a marine atmosphere, confirmed the promising protective properties, since no blistering, rusting, cracking and flaking was detected for most of the PMAs compositions evaluated. Additionally, the application of PMAs compositions (2 and 5) in automobiles proved their rust proofing, sealant, waterproofing and impact resistance properties, thus demonstrating the potential of these new coatings.

Acknowledgements

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References

1. E. López, F. J. Deive, M. A. Longo and M. A. Sanromán, *Bioprocess Biosyst. Eng.*, 2010, **33,** 929-935.
2. R. Vinai, A. Lawane, J. R. Minane and A. Amadou, *Constr. Build. Mater.*, 2013, **40**, 1088-1096.
3. R. Murillo, E. Aylón, M. V. Navarro, M. S. Callén, A. Aranda and A.M. Mastral, *Fuel Process Technol.*, 2006, **87**, 143-147.
4. F. Rozada, M. Otero, A. Morán and A. García, *J. Hazard. Mater.*, 2005, **124**, 181-191.
5. E.L.K. Mui, V.K.C. Lee, W. H. Cheung and G. Mckay, *Energ. Fuels, 2008,* **22**, 1650-1657.
6. V. González, F.J. Martínez-Boza, C. Gallegos, A. Pérez-Lepe and A. Páez, *Fuel Process Technol.*, 2012, **95**, 137-143.
7. K.D. Jeong, S.J. Lee, S. N. Amirkhanian and K.W. Kim, *Constr. Build.Mater.,* 2010, **24**, 824-831.
8. M. Isaac and I. Ori, Engineering Mechanics of Composite Materials. Oxford University Press: Oxford, (2005).
9. A.J. López, A. Ureña, M. D. López and J. Rams, *Surf. Coat. Technol.,* 2008, **202**, 3755-3763.
10. Directive 2000/53/EC of the European Parliament and of the Council of September 18, 2000 on end-of-life vehicles. Off J Eur Communities L269 (21.10.2000) p0034.
11. D. Lesueur, *Adv. Colloid. Interface Sci.*, 2009, **145**, 42-82.
12. F.J. Navarro, P. Partal, F. Martínez-Boza and C. Gallegos, *Fuel*, 2004, **83**, 2041-2049.
13. S.K. Palit, K. S. Reddy and B.B. Pandey, *J Mater.Civ. Eng., 2004,* **16**, 45-53.
14. F.J. Navarro, P. Partal, F. J. Martínez-Boza and C. Gallegos, *Polym. Test*, 2010, **29**, 588-595.
15. V. González, F.J. Martínez-Boza, F. J. Navarro, C. Gallegos, A. Pérez-Lepe and A. Páez, *Fuel Process. Technol., 2010,* **91**, 1033-1039.
16. H. Zhang, C. Shi, J. Han and J. Yu, *Constr. Build. Mater., 2013,* **40**, 1151-1155.
17. H. Zhang; H. Xu, X. Wang and J. Yu, *Constr. Build. Mater.*, 2013, **47**, 919-925.
18. J.R. Fields, Oxidized asphalt emulsions. United States Patent US Number 5,981, (1999) 632.
19. A. Tsuyoshi, H. Yoshimasa, N. Tadashi, S. Kazuhiko, I. Akira, I. Hiroyuki, Rubber modified asphalt type of water-proofing compositions. United States Patent US Number 5,891 (1999) 224.
20. D.V. Subotic, L. Kasaitskaya, S. Melancon, Asphalt compositions having improved properties and related coated method. United States Patent US Number 20130136855. 2013 May 30.
21. C.A. Echeverría, Composición de grasas para recubrimientos y procedimiento de obtención. Patente Cubana 143/94 (1994).
22. UNE-EN ISO 9227, "Ensayos de corrosión en atmósferas artificiales - Ensayos de niebla salina" (Madrid, Spain: Spanish Standardization and Certification Association [AENOR], 2007.
23. UNE-EN ISO 4628,"Pinturas y barnices. Evaluación de la degradación de los recubrimientos - Designación de la intensidad, cantidad y tamaño de los tipos más comunes de defectos - Parte 1 a Parte 6" (Madrid, Spain: Spanish Standardization and Certification Association [AENOR], 2003.
24. DIN EN ISO 6270-2, "Paints and varnishes - Determination of resistance to humidity - Procedure for exposing test specimens in condensation-water atmospheres" (Berlin, Germany: German Institute for Standardization [DIN], 2005.
25. ASTM D4799/D4799M, "Standard Practice for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Fluorescent UV, Water Spray, and Condensation Method)"(West Conshohocken, PA, USA: ASTM International [ASTM], 2013.
26. UNE-EN ISO 4624, "Pinturas y barnices - Ensayo de adherencia por tracción" (Madrid, Spain: Spanish Standardization and Certification Association [AENOR], 2003.
27. ASTM D2794, "Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)" (West Conshohocken, PA, USA: ASTM International [ASTM], 2010.
28. UNE-EN ISO 8565, "Metales y Aleaciones - Ensayos de corrosión atmosférica - Requisitos generales" (Madrid, Spain: Spanish Standardization and Certification Association [AENOR], 2012.
29. ISO 8407, "Corrosion of metals and alloys - Removal of corrosions products from corrosion test specimens" (Geneva, Switzerland: ISO International [ISO], 2009.
30. ISO 9226, "Corrosion of metals and alloys - Corrosivity of atmospheres - Determination of corrosion rate of standard specimens for the evaluation of corrosivity" (Geneva, Switzerland: ISO International [ISO], 2012.
31. ISO 9223, "Corrosion of metals and alloys - Corrosivity of atmosphere - Classification, determination and estimation" (Geneva, Switzerland: ISO International [ISO], 20012.
32. M. Echeverría, A. Rodríguez, C. M. Abreu and C. A. Echeverría, *Corrosion*, 2013, **69**, 1217-1224.
33. M.C. Pérez, Estudio de los sistemas de protección de las superficies metálicas expuestas a la intemperie, PhD thesis. Universidad de Santiago de Compostela (España) pp. 225 (1998).
34. William B. Coe, Asphalt-rubber compositions and systems and methods for preparing same. United States Patent Application US Number20150080504 (2015).

35. UNE-EN ISO 12944-5, "Pinturas y barnices - Protección de estructuras de acero frente a la corrosión mediante sistemas de pintura protectores - Parte 5: Sistemas de pintura protectores" (Madrid, Spain: Spanish Standardization and Certification Association [AENOR], 2008.

Fig. 1. View of the outdoor exposure test station

Fig. 2. Visual aspect of the PMAs samples after 1000 hours of exposure in a salt fog chamber

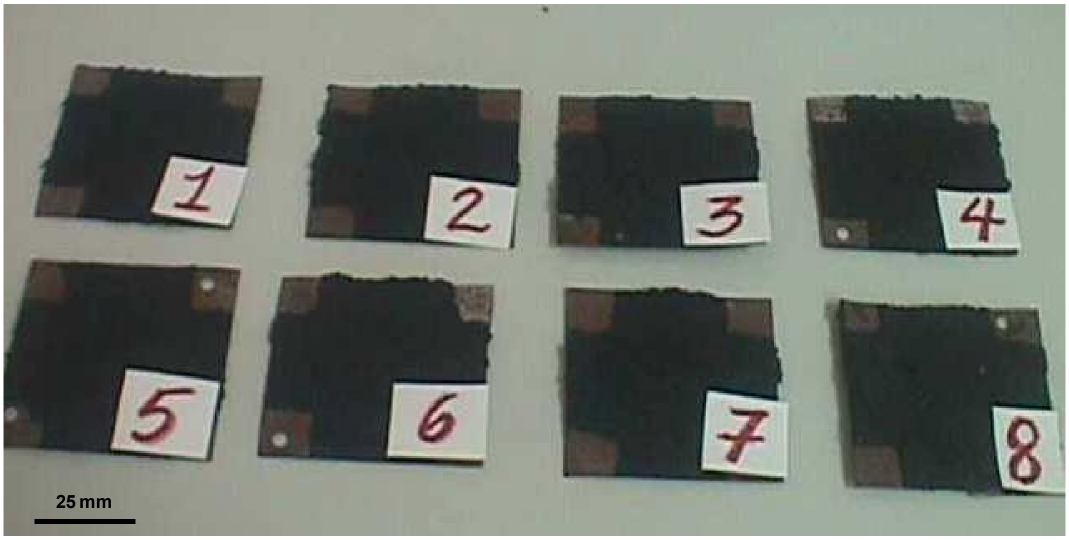


Fig. 3. Monthly weight loss evolution for carbon steel samples exposed to outdoor marine environment

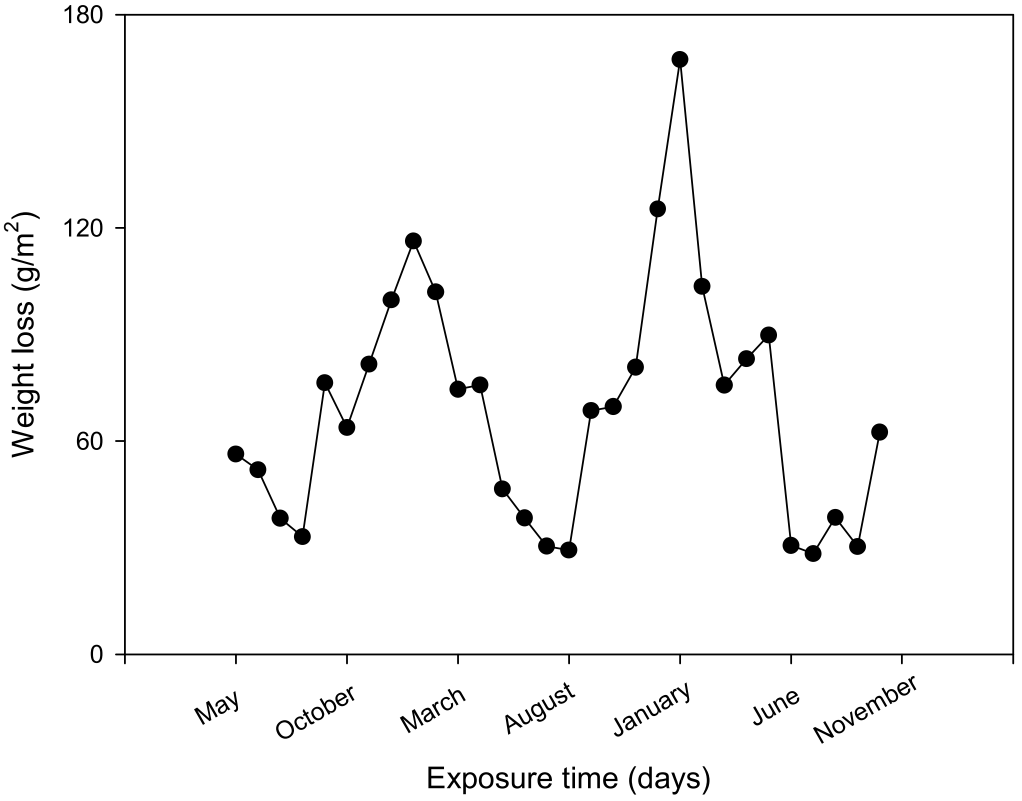


Fig. 4. Evolution of cracking in PMAs during 24 months of outdoor exposure

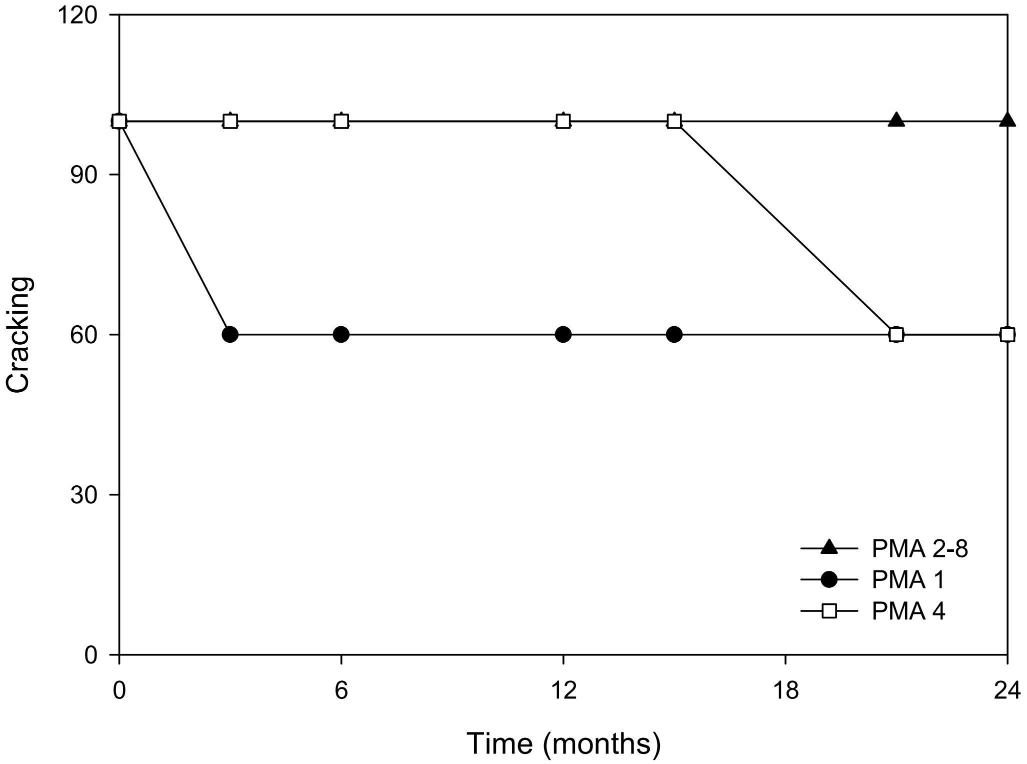
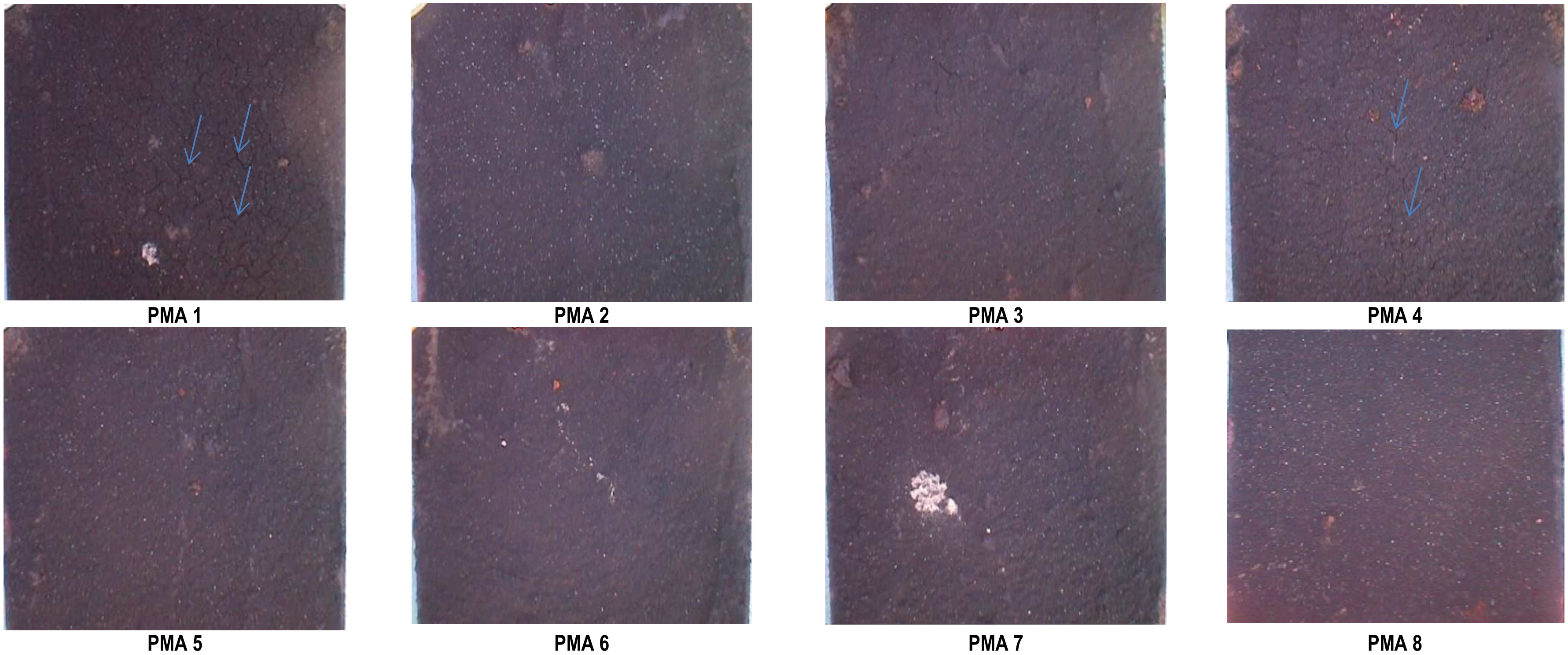


Fig. 5. Visual aspect of the PMAs after 24 months of outdoor exposure. Some cracks are identified with blue arrows



The wide of each figure is equivalent to 10 cm in the reality

Fig. 6. PMAs application A) in the sealing of a car floor (DISTIN 403), B) and C) as stone chip coating in the outside part of the car floor (DISTIN 403 L)

A)

B)

C)

Table 1. Chemical composition of the low carbon steel used

Elements (wt %)				
Fe	Mn	C	S	P
99.30	0.40	0.07	0.05	0.016

Table 2. Composition (%) of rubber in powder in each PMA variant and blending points (ºC)

Variants	**Powder rubber (wt.%)**	**Blending point (^{0}C)**
1	33.33	126
2	38.00	123
3	36.00	130
4	33.33	135
5	32.00	127
6	34.00	123
7	34.67	128
8	36.63	127

Table 3. Results of impact test for three different heights

Weight (kg)	**Height (cm)**	**Observations**
0.9	25	The material remains without visible changes and supports the load.
0.9	50	There is some detachment of the material.
0.9	100	Total release of the material. The base is observed.

Table 4. Average, maximum, minimum and standard deviation values of the weight loss (g/m^2) of the low carbon steel at different exposure times

	1 Month	**2 Months**	**3 Months**	**6 Months**	**12 Months**	**24 Months**
Average	68.93	122.26	179.55	305.82	565.25	1 024.70**
	-	-	-	-	671.95*	-
Maximun	167.37	255.35	270.32	420.31	580.35	1 024.70
Minimun	28.26	57.24	88.83	224.49	550.15	1 024.70
Standard deviation	33.35	27.43	35.10	30.40	21.35	0.00

*- Yearly average value starting the test in November, **-Yearly average value starting the test in May

Table 5. Identification of the numeric values assigned according to the UNE-EN ISO 4628-1 and equivalence with the scale detailed in 32

Mark[32]	Scale[1]	Adherence[1]	Blistering[1]	Rusting[1]	Cracking[1]	Flaking[1]
100	0	No release	No blistering	Ri 0	No cracks	0 %
80	1	< 5%	Scarce	Ri 1	Scarce	0.1 %
60	2	5-15%	2 S2-S5	Ri 2	2 S2-S5	0.3 %
40	3	15-35%	3 S2-S5	Ri 3	3 S2-S5	1 %
20	4	35-65%	4 S2-S5	Ri 4	4 S2-S5	3 %
0	5	> 65%	5 S2-S5	Ri 5	5 S2-S5	15 %

[1]UNE-EN ISO 4628-1: 2003

Table 6. PMAs* defects obtained after 24 months of outdoor exposure according to the UNE-EN ISO 4628-1

PMAs defects	**Time (months)**	**PMAs compositions**			
		1	**2**	**3**	**4**
Blistering	3	0	0	0	0
	6	0	0	0	0
	12	0	0	0	0
	15	0	0	0	0
	21	0	0	0	0
	24	0	0	0	0
Rusting	3	Ri 0	Ri 0	Ri 0	Ri 0
	6	Ri 0	Ri 0	Ri 0	Ri 0
	12	Ri 0	Ri 0	Ri 0	Ri 0
	15	Ri 0	Ri 0	Ri 0	Ri 0
	21	Ri 0	Ri 0	Ri 0	Ri 0
	24	Ri 0	Ri 0	Ri 0	Ri 0
Cracking	3	2 S(3)	0	0	0
	6	2 S(3)	0	0	0
	12	2 S(3)	0	0	0
	15	2 S(3)	0	0	0
	21	2 S(3)	0	0	2 S(3)
	24	2 S(3)	0	0	2 S(3)
Flaking	3	0	0	0	0
	6	0	0	0	0
	12	0	0	0	0
	15	0	0	0	0
	21	0	0	0	0
	24	0	0	0	0

*The PMAs (5-8) results not presented, are similar to PMAs (2-3) shown on the table.