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Novel Epoxy Coating Based on DMSO as a Green Solvent, Reducing Drastically the Volatile Organic Compound Content and Using Conducting Polymers As a Nontoxic Anticorrosive Pigment

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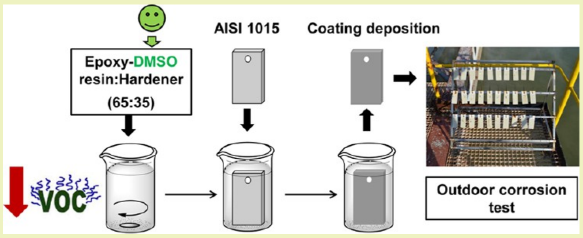
Supporting Information

ABSTRACT: This work reports novel anticorrosive epoxy coatings based on safer dimethyl sulfoxide solvent and free of zinc anticorrosive pigment. The latter was replaced by conducting polymers, as nontoxic anticorrosive pigments. The procedure used for their formulation, spectroscopic characterization, thermal and mechanical properties have been discussed and compared with those of conventional epoxy coatings. Furthermore, accelerated and long-term corrosion assays have evidenced that the new epoxy coatings protect steel from chlorine aggressive medium for 2880 h and for 2 years in atmospheric corrosive medium. Therefore, the results evidenced an excellent corrosion resistance, excellent application, and aesthetic appearance of the new coatings.



KEYWORDS: *Paint coatings, Conducting polymer, EIS, Carbon steel, Atmospheric corrosion*

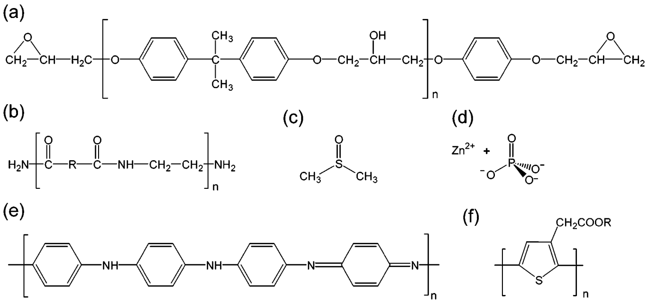
INTRODUCTION

Epoxy coatings form a class of high-performance material, chemically resistant, used in protective applications and mainly based on solvent-borne systems.[1] However, due to the persistent interest in the development of low or zero volatile organic compound (VOC) coatings with high performance, in the past few years innovative coatings technology, such as water-borne systems,[2−6] based on new resins and binders has emerged.[7−9] It is well-known, however, that water-borne systems involve a greater degree of difficulty for both formulator and applicator alike. Water-borne coatings are less tolerant to temperature changes and humidity and have less application in many corrosive mediums than solvent-borne systems.

High solids content solvent-borne epoxy coatings are low viscosity systems typically based on liquid diglycidyl ether of bisphenol A (DGEBA) (Scheme 1a) and bisphenol F (DGEBF) epoxy resins. Furthermore, they also require the employment of low viscosity amine curing agents, which must be compatible with liquid epoxies, and dimer-based polyamides, polyamidoamides, and phenalkamines for high solids epoxies. In contrast, water-borne epoxy coatings are prepared using solid and liquid epoxy resins dispersed in water.[7]

According to VOC regulations[10] and REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances),[11] some of the most important solvents and substances used in the formulation of epoxy coatings and classified as toxic will be withdrawn altogether. Some examples are 4,4′-diaminodiphenylmethane and dibutyl phthalate, which are currently under review and should probably be restricted for use.

Scheme 1. Main Components of the Epoxy Coatings Studied in This Work: (a) DGEBA Epoxy Resin; (b) Polyaminoamide Curing Agent; (c) DMSO; (d) Zinc Phosphate; (e) PAni-EB; and (f) PTE, Where R is a Methyl Group



Although not specifically excluded by REACH, the standards for toxic compounds have limited the use of many substances depending on the final product application. For example, the concentrations of xylene, butanol, phenol, and benzyl alcohol in organic coatings formulations are restricted by the assigned LCI (lowest concentration of interest) values, which express the

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critical levels of these toxic substances in a given environment (i.e., air, water, soil, or food). Thus, an LCI of 440 $\mu g/m^3$ has been assigned to benzyl alcohol for epoxy floor coatings applications, whereas the LCI of xylene and butanol for the same applications increases to 2200 and 3100 $\mu g/m^3$, respectively.

Replacement of volatile solvents is not a simple task due to, among other factors, the climatic conditions and pigment or additives formulations used for paints. Therefore, a completely VOC-free solvent-based system will never be offered. Nevertheless, the formulation of low emission epoxy coatings based in alternatives and nontoxic solvents is necessary and extremely urgent.[12] In this way, dimethyl sulfoxide (DMSO) is a good candidate to replace toxic solvents[13−16] due to its high boiling point (189 °C at 760 mmHg) and a very low vapor pressure (0.6 mmHg at 25 °C). DMSO offers many benefits to be used in paint formulations, despite the fact that it is not considered as a green solvent, like water or dimethyl carbonate.[17] According to US Environmental Protection Agency (EPA), this solvent is classified as nontoxic with no risk for the human health.[18] DMSO is able to solubilize a wide range of polymers, including epoxy resins, at room temperature. Moreover, DMSO is miscible with all common solvents such as aromatics, ketones, acetate, and it is also completely miscible in water, allowing its use in both solvent- and water-borne coatings. Furthermore, this solvent is often recycled by its users, limiting discharges. DMSO is present in some industrial wastewaters and is readily biodegradable.

Another aspect to be discussed in this paper, which currently represents a handicap of increasing interest, is the replacement of toxic inorganic anticorrosive pigments on protective coatings. In order to provide higher durability and protection to metal structures, protective coatings usually incorporate inorganic anticorrosive pigments based on zinc metallic or zinc-phosphate. Nowadays, particular attention has been paid to the use of zinc derivatives in organic coatings. Accordingly, Lima-Neto et al.[19] proposed that zinc phosphate should be classified as "not hazardous" for human health but "very toxic" for the aquatic environment. Heavy-duty primers to marine, offshore, and structural steelwork employ almost 80 wt % zinc dust in their formulations while light-duty epoxy formulations for industrial environments use 30−40 wt % zinc phosphates as an anticorrosive pigment. Therefore, cathodic protection of vessels or maritime platforms is an important source of contamination of aquatic life. The European Community restricted the use of zinc through a regulation (Directive 76/464 EC, codified as 2006/11/EC),[20] giving place to intense research aimed to look for alternative pigments to replace zinc derivatives.

In this work we apply the principles of "green chemistry" and engineering to design a novel epoxy formulation based on DMSO, as a nontoxic and environmental friendly solvent, combined with organic additives based on conducting polymers (CPs), as nontoxic anticorrosive pigments. Thus, our aim is essentially focused on the formulation of solvent-borne epoxies made of bisphenol A epoxy resin and polyamide curing agent[21] with low VOC emission and efficient anticorrosive performance. Structural and morphological characterization of the coating based on DMSO have been carried out, results being compared with those obtained for the same epoxy primer but based on xylene, a common volatile solvent used in commercially available primers. In order to evaluate the protection performance achieved by the novel epoxy coating, both accelerated corrosion assays in the laboratory and long corrosion exposure of steel painted panels in an aggressive industrial medium (i.e., field corrosion assays) have been performed. The modifications introduced in the paint formulation provide important benefits to manufacturers. Among them, the following ones deserve special mention: (i) significant reduction of health hazards (i.e., DMSO is considered a "green-solvent"); (ii) CPs are considered nontoxic materials due to their very low concentration in the coating formulation (0.3−1.0 wt %) compared to zinc compounds; and (iii) reduction of the formulation cost and the coating weight, caused by the substitution of high concentrations of inorganic additives for very low concentrations of organic additives. It should be remarked that the latter provokes a reduction of combustible consumption in naval applications due to the reduction of the coating specific density.

■ EXPERIMENTAL SECTION

Materials. Solid epoxy resin Epikote 1001 ($M_n \sim 800$, WPE 400−500) and polyaminoamide curing agent Crayamid 195 × 60 (HEW 240) were supplied by Cray Valley Spain. The organic anticorrosive additives used in this work were polyaniline emeraldine base (PAni-EB) and poly[2,2′-(3-methylacetate)thiophene] (PTE). The first was supplied by Sigma-Aldrich, and the latter was synthesized in our laboratory, accordingly to the experimental procedure described by Osada and co-workers.[22] All pigments and rheological additives were purchased from different suppliers, as detailed in the next section. The main solvents (dimethyl sulfoxide 99.5% and *m*-xylene) were supplied by Panreac Química S.A. Corrosion experiments were performed using DIN CK15 (AISI/SAE 1015) steel panels (chemical composition: Fe 99.13−99.57%, C 0.13−0.18%, Mn 0.30−0.60%, S ≤ 0.050%, and $P \leq 0.040\%$) with dimensions of 120 mm × 40 mm × 2 mm as the metallic substratum.

Formulation and Preparation of the Epoxy Coating Using DMSO as Solvent. The chemical structure of the main components of the epoxy coatings prepared in this work is displayed in Scheme 1. Three different bicomponent epoxy formulations, which differ in the anticorrosive additive, were prepared. More specifically, these formulations contained 10 wt % zinc phosphate (epoxy−DMSO/Zn), 0.3 wt % PAni-EB (epoxy−DMSO/PAni), or 1.0 wt % PTE (epoxy−DMSO/PTE) as anticorrosive additive. Thus, the inorganic additive of the former was substituted by a very small concentration of organic CPs in the latter two. The epoxy/amine ratio is 1.4−1.6, and the PVC/CPVC ratio (pigment volume concentration/critical pigment volume concentration ratio) was maintained at 0.65−0.70 in all cases.

For the first formulation, 75 g epoxy resin (Epikote 1001, Hexion Specialty Chemicals, Inc.) was initially dispersed in 25 mL of DMSO (Panreac Química S.A.). Next, 20 wt % such epoxy dispersion, 5 wt % titanium dioxide (white oxined, Europigments), 10 wt % zinc phosphate (Nubiola), 20 wt % barite (Barium sulfate, Viaton Industries Ltd.), 12 wt % talc (Industrial Talc FF, T3Química), 0.23 wt % Aerosil 200 (Degussa AG), 1 wt % Antiterra U (BYK Chemie GmbH), 0.7 wt % BYK-500 and BYK-525 (BYK Chemie GmbH), and 19 wt % DMSO were mixed and dispersed at 15 000 rpm for 20 min with a Dispermat disperser model TU. After the mixing and dispersion, the formulation was ground in a batch mill APS 250 provided with zirconium oxide balls to reduce the particle size below 40 μm. After milling at 7000 rpm for 20 min, component A of the epoxy paint was obtained. Then, 12 wt % of component B, which consisted on a polyaminoamide (Crayamid 195 × 60, Cray Valley), was added to component A and stirred for 5 min with the disperser.

The epoxy−DMSO/PAni primer was prepared by mixing 19 wt % epoxy resin, which was previously dispersed in DMSO, 7 wt % titanium dioxide, 24 wt % barite, 12 wt % talc, 0.27 wt % Aerosil 200, 1 wt % Antiterra U, 1 wt % by weight BYK-500 and BYK-525, and 20 wt % DMSO. The dispersion process was identical to that described for the epoxy−DMSO/Zn formulation. The addition of the organic anticorrosive pigment required special attention, since PAni-EB is a solid with a remarkable tendency to agglomerate when contacted with

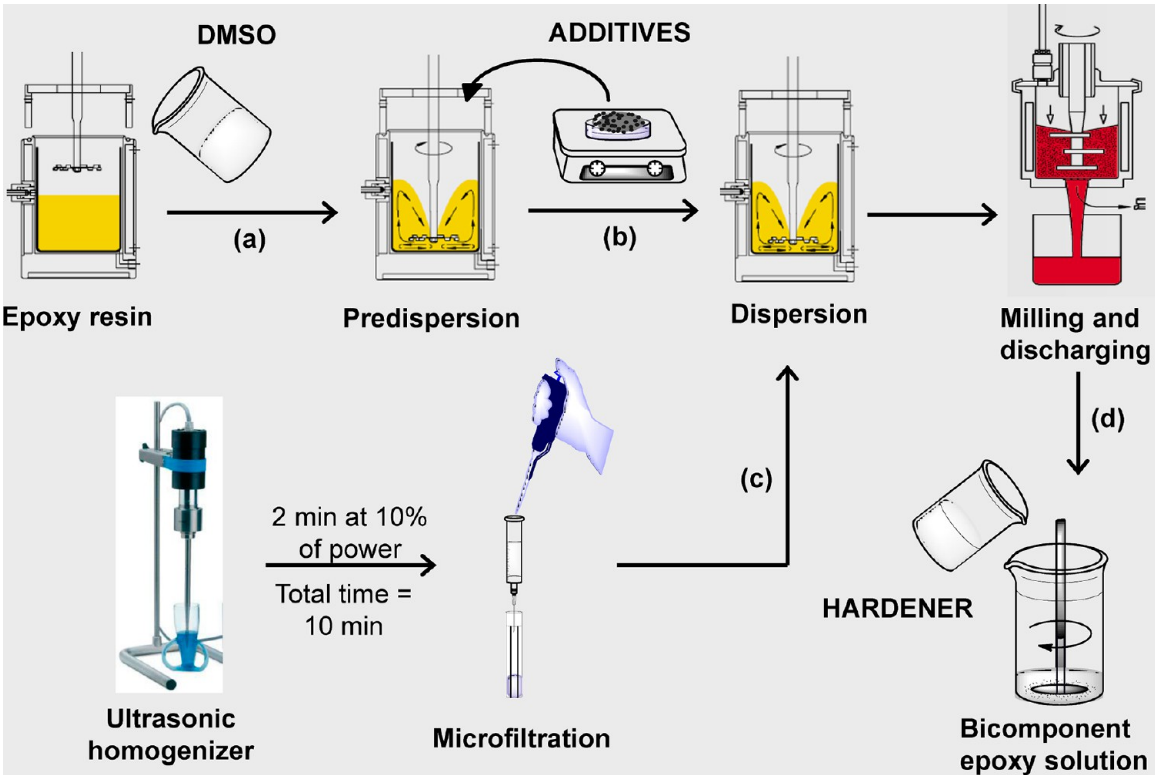

Figure 1. Schematic representation of the strategy used in this study for the preparation of the epoxy coatings based on DMSO, as safer organic solvent, and conducting polymers, as nontoxic anticorrosive pigments: (a) predispersion of the epoxy resin in DMSO; (b) addition of pigments and rheological additives; (c) preparation of micrometric particles of conducting polymer in DMSO before its addition to the paint formulation; and (d) addition of polyaminoamide hardener component.

a liquid medium. In order to incorporate the PAni-EB to the paint formulation (component A), it was necessary to reduce the particle size using an ultrasonic homogenizer. After the particle size reduction and microfiltration, 0.3 wt % PAni-EB was added very slowly to the paint formulation. The employment of PAni-EB and PTE as anticorrosive pigments in alkyd and epoxy primers is a new technology recently patented in our laboratory;[23] the complete dispersion procedure is described in the patent. After component A preparation, 12 wt % of the polyaminoamide (Crayamid 195 × 60, Cray Valley) used as component B was added and stirred for 5 min with the disperser (Figure 1).

The epoxy−DMSO/PTE paint was prepared by mixing 20 wt % epoxy resin, which was previously dispersed in DMSO, 5 wt % titanium dioxide, 1 wt % PTE, 20 wt % barite, 12 wt % talc, 0.23 wt % Aerosil 200, 1 wt % Antiterra U, 0.7 wt % BYK-500 and BYK-525, and 19 wt % by weight DMSO. The dispersion procedure was identical to that explained for PAni-EB (also detailed in ref 19), the mixing ratio of components A and B being also maintained.

After induction time of 30−40 min, the paint coatings were applied by immersion of 120 mm × 40 mm × 2 mm steel panels, which were previously degreased with acetone and polished with zirconium balls accordingly to standard method UNE-EN-ISO8504,[24] into the formulations. The coatings were dried on air for 1 week before corrosion tests. The dry film thickness (DFT), which was measured with a machine model Mega-Check pocket NFE from Neurtek S.A company, was 90 ± 15 μm (one coat).

Preparation of casting films for physical−chemical characterization was carried out using two procedures: (i) drying on air at room temperature for 7 days (RT) and (ii) applying a postcuring treatment at 120 °C for 24 h in an oven (HT).

Characterization Methods. Structural characterization of the coating films was performed using a Jasco 4100 FTIR spectrometer with a resolution of 4 cm^{-1} in a wavenumber range of 4000−600 cm^{-1}. Samples were placed in an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma). Differential scanning calorimmetry (DSC) was performed using a TA Instruments Q100 series equipped with a refrigerated cooling system (RCS) operating at temperatures from −90 to 550 °C and employing a heating rate of 10 °C/min. Experiments were conducted under a flow of dry nitrogen with a sample weight of approximately 5 mg, and calibration was performed with indium. On the other hand, thermogravimetric analyses (TGA) were carried out with a Q50 thermogravimetric analyzer of TA Instruments at a heating rate of 20 °C/min under nitrogen atmosphere and a temperature range from 20 to 600 °C. Finally, properties typically used to determine the mechanical characteristics of paints (i.e., Youngs modulus, tensile strength, and elongation at break) were evaluated using stress−strain assays with a Zwick Z2.5/TN1S testing machine. Regular films were prepared by casting at room temperature (RT) and after postcured treatment (HT), described on the above section. Plate samples with a length of 30 mm, a width of 3 mm, and a thickness of 250−350 μm were cut out from the films for stress−strain experiments. The deformation rate was 0.8 mm/min. A total of 10 independent measurements were performed for each paint film, and mechanical parameters reported in this work correspond to the average of such measurements.

Electrochemical Impedance Spectroscopy. In order to evaluate the response as anticorrosive coatings of the paints prepared in this work as a function of time, electrochemical impedance spectroscopy (EIS) was performed in aqueous 3.5% NaCl solution at open circuit potential (OCP). The DFT is an important parameter in EIS assays and was maintained at 90 ± 15 μm for all coatings. Two different samples were evaluated; epoxy−DMSO/PTE and epoxy-xylene/PTE, and two steel painted panels were considered for each one. The working electrode employed was the steel panel (AISI/SAE 1015) used as metallic substratum with an area of 0.7854 cm^2. Platinum and silver|silver chloride (Ag|AgCl) electrodes were used as counter and reference electrodes, respectively. EIS measurements were performed with a potentiostat Autolab PGSTAT 302N. The amplitude of the EIS perturbation signal was 10 mV, the frequency ranged from 10^5 to 10^{-2} Hz taking 70 frequencies per decade. All the EIS analyses were conducted under potentiostatic conditions.

Field Corrosion Test. Test panels of carbon steel (120 mm × 40 mm × 2 mm) were coated with two paint systems: epoxy priming paints prepared with DMSO nonvolatile solvent as first coat and commercial epoxy paint (Hempadur epoxy primer 15300 and curing agent 95040) as topcoat. The DFT of first coat varied from 80 ± 10 to 150 ± 20 μm and the topcoat presented a DFT of 190 ± 20 μm after 1 week of drying at room temperature (higher than 20 °C). All test panels were placed in a stainless steel rack (Figure 2a–b), specially designed for the panels dimensions described before and moved to an industrial corrosive zone over an open brine tank for chlorine gas production (Figure 2c). The concentration of the brine tank is about 240 g/L of NaCl, and the temperature during the winter months is around 35 °C; whereas in the summer months, the temperature reach almost 60 °C. Field corrosion assays were performed in Hispavic Ibérica S.L., which is an important company from Solvay S.A Group and PVC manufacturer. This company is located at Martorell, a Spanish city 30 km from Barcelona.

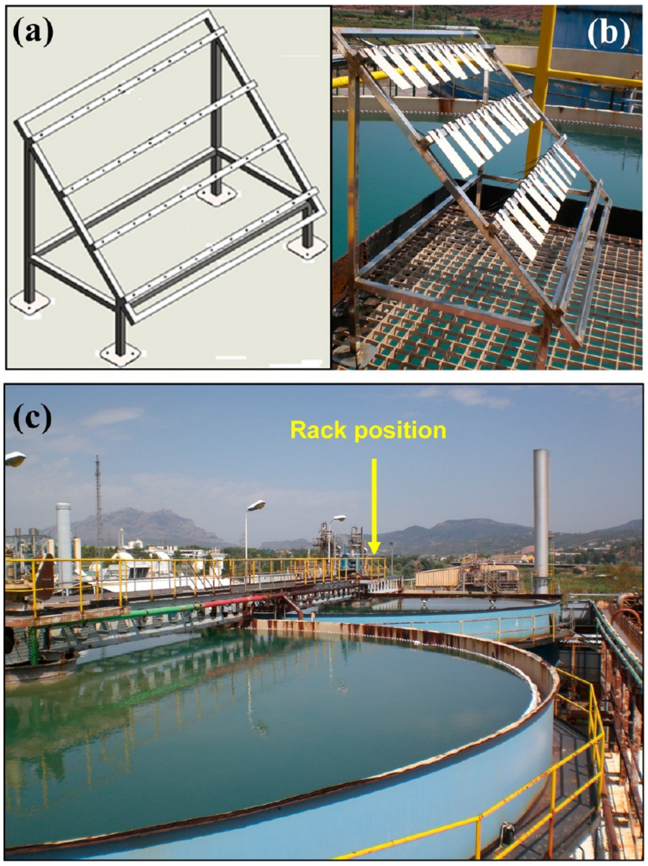

Figure 2. (a) Rack prototype with scale dimensions of 1:20. (b) Photography of stainless steel AISI 316L rack constructed as samples holder. (c) Open brine tanks at Hispavic Ibérica S.L., located at Martorell (Spain). Arrow indicates the position of rack for long-term corrosive assays.

■ RESULTS AND DISCUSSION

Epoxy–DMSO Formulation: Advantages and Disadvantages. Organic coatings are a complex mixture of binder, which is the main constituent, pigments, solvents, and additives. In order to replace xylene by DMSO as solvent in two-component epoxy coating (i.e., composed by an epoxy resin and a curing agent), the compatibility between the Epikote resin 1001 (solid epoxy resin produced from bisphenol A and epichlorohydrin) and DMSO was evaluated. Accordingly, an epoxy–DMSO solution was prepared using the same conditions that the preparation of a commercial available epoxy resin based on xylene as main solvent. Due to the high viscosity of the Epikote 1001, homogenization of the solid resin with a low concentration of DMSO required 6 h of magnetic stirring at room temperature (higher than 20 °C).

After this, the solubility in DMSO of the CPs, PAni-EB, and PTE, and the zinc phosphate dihydrate used as anticorrosive pigments was examined. As expected, zinc phosphate dehydrate was very easy to disperse in DMSO due to the high miscibility of this solvent in water. On the other hand, the strong aggregation tendency and poor solubility of CPs in common solvents are well-known. However, PAni-EB was ease to dissolve in DMSO, reasonable dispersion being achieved when the PAni-EB powder size was reduced applying 20 min of ultrasound stirring. Previous works demonstrated that chloroform,[25] *N*-methyl pyrrolidone,[26] and xylene[27] are solvents able to disperse various forms of polyaniline. Nevertheless, as they are not green solvents, they have not been considered for the formulation of sustainable paints.

CPs based on polyaniline and polythiophene have been previously dispersed in DMSO with ultrasounds before of their incorporation to the paint formulation (Figure 1). In opposition to PAni-EB, PTE has no tendency to agglomerate, even though it is very important reduce its particle size to achieve a well dispersed solid in the liquid paint. The particle size of PTE in DMSO after microfiltration is around 141.05 ± 38.88 nm, measured by Static Light Scattering with a Vasco Particle Size Analyzer. PTE behaves as an anticorrosive and as pigment, providing yellow color to the final paint. PAni-EB offers lilac-colored films.

In order to compare with conventional epoxy formulations, epoxy–xylene formulations with the same epoxy/amine and PVC/CPVC ratios were prepared. The volatile and toxic aromatic hydrocarbon solvent content of the latter xylene formulations (260 g/L) drastically decreased to 70 g/L in epoxy–DMSO based paint. Thus, complete elimination of xylene as solvent and methyl isobutyl ketone (MIBK) or butanol as cosolvents from epoxy formulation was not possible due to the high insolubility of the curing agent in DMSO and as well as its high viscosity parameters. New directives related with the VOC content in paints and varnishes were implemented in the last European Council of the Paint, Printing Ink, and Artists' Colors Industry (CEPE); the maximum VOC content for chemically curing anticorrosive primers was established as 290 g/L.[28] Therefore, the formulations described in this work not only use a less toxic solvent with very low releases into the environment but also adhere to the European Commission regulations. On the other hand, replacement of zinc phosphate anticorrosive additive by a low concentration of CP, either PAni-EB or PTE, results in a decrease of the coating density: from 1370 kg/cm^3 for epoxy–DMSO/Zn to 1100 and 1160 kg/cm^3 for epoxy–DMSO/PAni and epoxy–DMSO/PTE coatings, respectively. This represents an important benefit for many applications.

However, formulation of such coatings is not an easy task and some experimental problems must be overcome. When xylene is substituted by DMSO, the coating maintains its low-temperature curing (discussed in the next section), but the time of dry to touch increases from 6 to 8 to 48 h at 20 °C. This drawback can be overcome by applying surface thermal treatment to accelerate the solvent evaporation and curing process. Another handicap is the service temperature, which must be higher than the DMSO melting point of 18.45 °C. This limitation affects both the paint fabrication process and the use of the paints. Regarding the former, problems can be easily avoided if manufacturers use a dissolver system with a double-wall container with slight heating (i.e., to minimize the risk of epoxy base resin solidification inside the container). However, the use of these new paints below 19–20 °C is not recommended, and customers should avoid their application in winter or in Nordic countries.

Spectroscopy and Thermal Characterization. Epoxy systems are preferred materials chosen for application as protective coatings due to their excellent barrier properties, high chemical resistance to common solvents, high thermal stability, and good mechanical properties. The properties of these thermosetting polymers are highly dependent on the curing process. For this reason, paint manufacturers always indicate some physical constants and application details related to the curing process, (i.e., the mixing ratio between the epoxy base resin and the hardener, the time and temperature for fully cured material, or the dry film thickness). Two component epoxy–xylene primers are usually considered to be fully cured without further thermal treatment after 7 days at 20 °C. We assumed that replacement of xylene by DMSO will affect the curing process of the epoxy system.

We compares the FTIR spectra obtained for epoxy–xylene RT (Figure S1.c, see the Supporting Information) and epoxy–DMSO RT films, which were prepared by solvent casting at room temperature and allowed to dry for 7 days without vacuum (Figure S1.b), with the epoxy–DMSO HT films that were prepared by casting and cured at 120 °C for 24 h (Figure S1.a). We observed that the polymerization of epoxy terminal groups from DGEBA and polyaminoamide was complete, independently of both the solvent and application of the thermal treatment at 120 °C. The absence of the absorption of epoxy ring (~915 cm^{-1}) and the presence of OH and C–N groups corroborate the conversion of epoxy group into the corresponding polymer and the cross-linking process.

Another aspect that deserves consideration is the evaporation of DMSO from the polymer matrix in films. Although the DMSO absorption bands are not present in the FTIR spectra in epoxy–DMSO RT or HT coatings (see Table 1, Supporting Information), complete evaporation from the polymer films cannot be ensured. Indeed, we assumed that a small amount of solvent remains trapped inside the epoxy polymer chains because of its very high boiling point. Table 1 summarizes the main absorption bands obtained for the epoxy coatings studied in this work, comparison with xylene[29] and DMSO[30] pure solvents being also provided. It is well-known that the characterization of coatings by FTIR spectroscopy is a difficult task due to the presence of many additives and pigments. Supporting Information Figure S1 allows us to distinguish the presence of silicates and phosphates additives in the complex composition by the presence of Si–O and P–O bands at ~1000 cm^{-1}, whereas the identification of CPs is difficult due to their very low concentration in the paint formulation (0.3 wt %), as reported in previous works.[31]

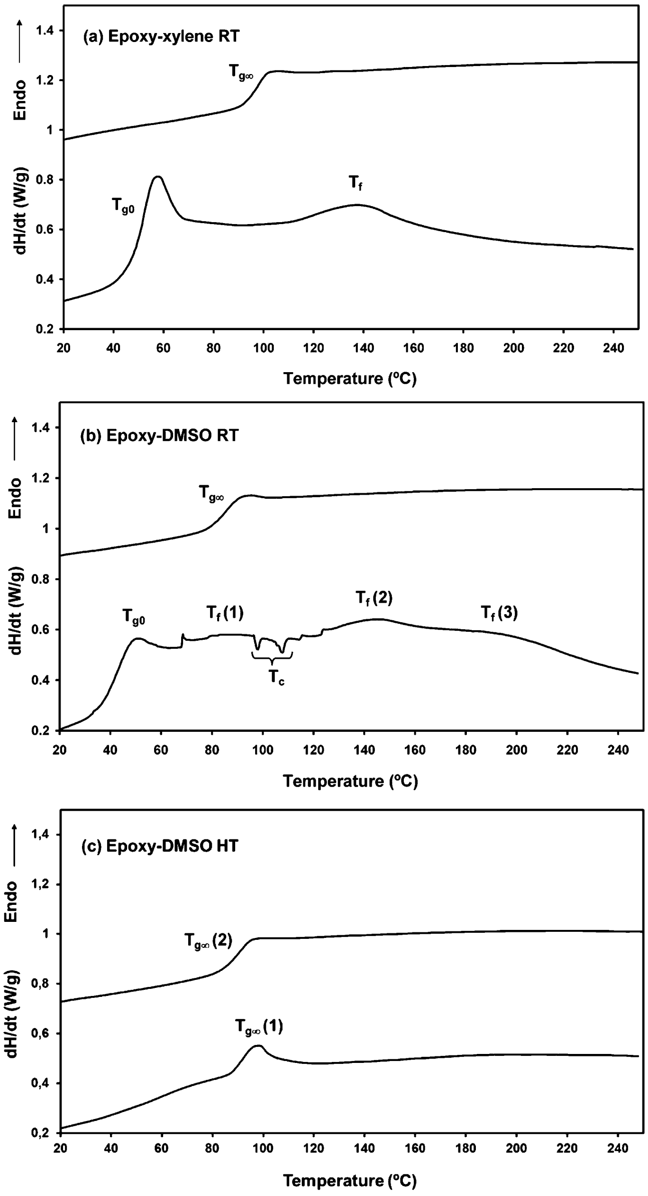

Figure 3. DSC curves showing the glass (T_g), crystallization (T_c), and melting (T_f) transitions associated with (a) epoxy–xylene RT; (b) epoxy–DMSO RT; and (c) epoxy–DMSO HT. Heating rate 20 °C/min; first heating down; and second heating up.

Thermal analyses revealed important differences between the xylene and DMSO compositions. Figure 3 displays the calorimetric curves for the epoxy–xylene RT and epoxy–DMSO RT after 7 days of evaporation at room temperature, and the epoxy–DMSO HT with curing treatment at 120 °C for 24 h. As it can be seen in the first heating, the epoxy–xylene RT (Figure 3a) has a glass transition (T_{g0}, without further thermal treatment) at 52.4 °C and a fusion process between 120 and 160 °C, whereas the epoxy–DMSO RT (Figure 3b) has a T_{g0} at 43.6 °C and many fusion and crystallization processes at temperatures higher than 67 °C. This phenomenon is associated with our previous assumption that an amount of DMSO remains inside the polymer matrix, the peaks observed being associated to the DMSO evaporation and further polymerization of the epoxy coating. Both xylene and DMSO affect the thermal behavior of epoxy coatings, making the complete polymerization of the epoxy difficult (i.e., they prevent the complete curing of the films). Thus, additional peaks related to the fusion process are not expected to appear in completely epoxy resins. Within this context, DMSO behaves worse than xylene because some molecules of the former solvent remain trapped inside the polymer matrix.

In the second heating process, DMSO induces a lower $T_{g\infty}$ (where $T_{g\infty}$ corresponds to the glass transition of a sample fully cured) for the epoxy system than for xylene (i.e., 87.0 and 91.4 °C, respectively). This behavior suggests that the solvent participates in the cross-linking of polymer chains, acting as a plasticizer and improving the postcuring process. However, this observation only appears after application of additional isothermic treatment. These results indicate that the thermal treatment at 120 °C is not necessary for the paint application since the T_{g0} of the epoxy system (i.e., around 50 ± 7 °C) is higher than room temperature, evidence that the epoxy polymer is partially cured. Accordingly, no further isothermal treatment is needed if the mechanical and barrier properties of the films are good enough to enable their use as protective coatings.

Finally, Figure 3c shows the DSC curves for the epoxy–DMSO film treated at 120 °C for 24 h. In this case, the epoxy is free of DMSO, the film being fully cured. Thus, the $T_{g\infty}$ values obtained from the first and second heating curves, $T_{g\infty}$ = 92.2 and 92.4 °C, respectively, are very similar to that achieved for the epoxy–xylene RT film ($T_{g\infty}$ = 91.4 °C, Figure 3a).

The DSC curves of coatings modified with CP showed the same $T_{g\infty}$ values that the epoxy system with zinc phosphate after complete curing process. However, the coatings without isothermal treatment present a broad fusion peak from 90 to 200 °C, which has been associated to the covalent interaction between the epoxy resin and PAni or PTE. CPs are amorphous materials able to interfere with the crystalline domains of polymer chains, as recently reported for systems based on mixtures of thermoplastic polyurethane (TPU) and PTE,[32] affecting the fusion process.

The thermal stability of the epoxy resins formulated with DMSO and modified with CPs has been evaluated by TGA. Figure S2 (Supporting Information) compares the TGA curves for the epoxy resins modified with zinc phosphate, PAni-EB or PTE (epoxy–DMSO/Zn, epoxy–DMSO/PAni, and epoxy–DMSO/PTE resins, respectively) but without containing inorganic additives and pigments. Thus, these systems are not final paint coatings, as is reflected by the low amount of solid contents at 600 °C. All films were first cured at 120 °C for 24 h to ensure the elimination of DMSO and to obtain a cross-linked material. As expected, the decomposition temperatures are very high in all cases: 421, 433, and 437 °C for the epoxy–DMSO/Zn, epoxy–DMSO/PTE, and epoxy–DMSO/PAni resins, respectively. Interestingly, the addition of PAni-EB and PTE produced a small increment in the thermal stability of the epoxy resin, which has been attributed to the interaction of the amine and ester groups with the polymer chains. The solid content of the modified epoxy resins at 600 °C is lower than 15% whereas the solid contents typically observed for epoxy paints (with additives and pigments) range from 30% to 45%.

Mechanical Properties of the Epoxy–DMSO Coating Compared to Epoxy–Xylene. The Young's modulus, tensile strength and strain to break of the epoxy coatings prepared using DMSO as solvent differ significantly from those of conventional paints prepared in xylene. Figure S3 (Supporting Information) shows the stress–strain curves for the coatings prepared at RT and HT. In general, epoxy–xylene films have high tensile strength (σ_{max}: 25–32 MPa) and very low elongation at break ($\varepsilon_{\sigma max}$: 2.7–3.4%) when deformed at room temperature, as is typically observed in epoxy systems.[33] In contrast, epoxy–DMSO films present very low tensile strength (σ_{max}: 3–5 MPa) and very high elongation at break ($\varepsilon_{\sigma max}$:121–189%), independently of the curing temperature. Therefore, DMSO solvent produces a significant reduction of the elastic modulus (E: 5–7 MPa) and an enhancement of ductility, this behavior being similar to that observed for some thermoplastics.[33]

It should be mentioned that epoxy–DMSO/Zn films were not assayed because of its extremely high brittle behavior. Unfortunately, we were unable to cut the films to obtain the test samples. As this is the first anticorrosive epoxy paint prepared with zinc phosphate prepared with DMSO as solvent, the reasons of this brittle behavior are not definitively clear. However, we assume that it comes from the high amount of zinc phosphate in the paint formulation (10 wt %), which is significantly higher than in epoxy–DMSO/PAni and epoxy–DMSO/PTE. These results indicate that PAni-EB, PTE, and DMSO interact favorably with the epoxy system giving a plastic behavior with less brittle properties than conventional epoxy paints prepared with xylene.

Comparison of Epoxy–DMSO/PTE and Epoxy–Xylene/PTE Anticorrosive Performance. Several authors investigated the failure mechanism of different coating systems by multifrequency ac impedance measurements.[19,26,34−37] This procedure allows to monitor the behavior of coated surfaces giving valuable information about both coating degradation and the coating resistance to protect the metal surface. The corrosion behavior of uncoated and epoxy coated steel panels was evaluated by electrochemical impedance spectroscopy (EIS) in 3.5 wt % NaCl aqueous solution considering different immersion times (Figure 4). The corrosion potential (E_{OCP}), coating resistance (R_p) at high frequencies, and coating capacitance (C_c) derived from impedance curves are listed in Table 2 (see the Supporting Information).

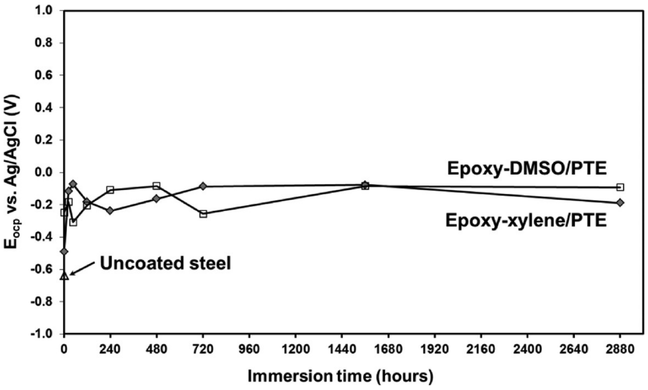

Figure 4. Evolution of the corrosion potential (E_{ocp}) with the immersion time.

The E_{OCP} of unprotected mild steel is very low and negative (−0.638 V), whereas the protected metal has more positive values. More specifically, epoxy–xylene/PTE and epoxy–DMSO/PTE showed similar corrosion potential over 4 months (2880 h), as is reflected in Figure 4. Accordingly, both coatings exert the same protection compared to the uncoated steel, maintaining almost constant E_{OCP} values during the four months of exposure in NaCl 3.5%.

Figure 5 shows the Nyquist plot at various immersion time for the uncoated steel and coated with epoxy–DMSO/PTE and epoxy–xylene/PTE. Uncoated carbon steel has a high

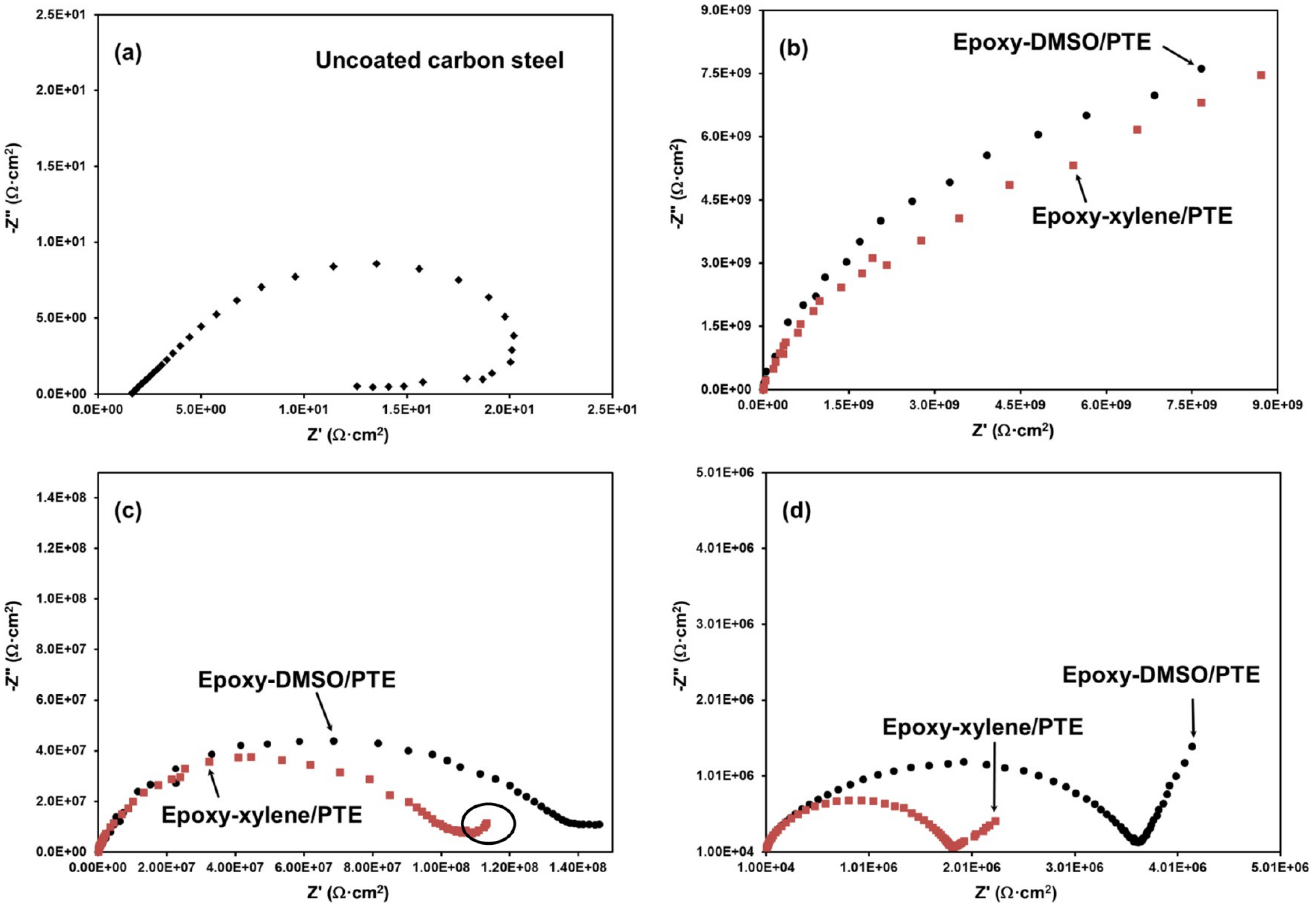

Figure 5. Nyquist plot of mild steel after 1 h of immersion in NaCl 3.5% (a) and mild steel coated with epoxy−DMSO/PTE and epoxy−xylene/PTE after 1 h (b), 20 days (c), and 2 months (d) of immersion in NaCl 3.5%.

adsorption and desorption of species at metal surface related to active dissolution sites at the low-frequency region, which can be appreciated on the Figure 5a. However, coated steel substrates show a highly resistive behavior with impedance values of about 10^9−10^{10} Ω·cm^2 at high frequencies (Figure 5b), these values being comparable to those obtained for other protecting coatings.[37]

In organic coatings systems, the pore resistance (R_p), which is associated to the coating resistance, usually decreases with time, as is evidenced in Table 2 (of the Supporting Information). Although epoxy systems present high chemical resistance to both solvents and water, they are porous materials, and therefore, aggressive electrolytes are able reach the metal surface in a short time. Fortunately, the anticorrosive additive offer an additional resistance to metal corrosion, acting as sacrificial anode or promoting a passive layer between the metal and coating interface. The two PTE-containing epoxy formulations studied in this section, which differ in the solvent, show similar protection. This result indicates that the solvent does not affect the permeability of the coating. Indeed, differences in coating resistance must be attributed to the thickness of the coatings, which is higher for the epoxy−DMSO/PTE (107 ± 12 μm) than for the epoxy−xylene/PTE paint (72 ± 8 μm).

EIS tests revealed that both coatings have only two time constants (σ) at initial exposure in NaCl (from 1h to 20 days), both overlapped in the Nyquist plot. The complete semicircle, from high to low frequency range, represents the excellent barrier protection and high impermeability of the epoxy coating. The coating resistance values (R_p) gradually decreased (from 20×10^9 to 3×10^6 Ω·cm^2) and the coating capacitance (C_c) gradually increased (from 1.2×10^{-10} to 3.0×10^{-9} F·cm^2·s^{n-1}) with the immersion time (Table 2, Supporting Information). As the NaCl diffusion inside the coating is unavoidable, a third time constant (σ) appears after 20 days of immersion test (Figure 5c). Indeed, this is detected by a slight increase of a second semicircle in the low frequency zone. This can be interpreted by the time required to initiate the development of other significant interface under the coating, like passive layers or oxide corrosion products from pitting or deposited substances. However, this is a good result taking to account that the coating resistance is still high after 4 months (~2×10^6 Ω·cm^2; data not shown). Comparison of the EIS results obtained for these same epoxy systems with those recently reported for PTE-containing alkyd systems indicates that the latter start to corrode earlier, the third time constant being observed after 7 days only.[38]

After 4 months in contact with sodium and chloride ions, the Nyquist curves show only three time constants (Figure 5d), showing evidence that the coating systems still protect the metal. No pitting signal was visually observed inside the coating, indicating that the third semicircle appeared after 20 days is not due to an aggressive oxide product formation. EIS results are in excellent agreement with outdoor industrial corrosive assays performed over an open brine tank (see next section).

It should be mentioned that epoxy−DMSO/Zn films were not assayed because of their extremely brittle behavior (one coat application). In spite of this, the performance of this formulation was checked in the outdoor assays (see next section). In regard to the epoxy−DMSO/PAni, results (not shown) indicate that this coating offers lower protection than the PTE-containing systems (i.e., lower coating resistance and higher capacitance than epoxy/PTE). However, these results are been omitted because the anticorrosive properties of epoxy/PAni systems were extensively studied in previous works.[25,27,31,38]

Checking the Effectiveness of the Epoxy−DMSO Anticorrosive Paint in Outdoor Corrosion Tests. The phenomenology of blister formation and growth on coated mild steel exposed to outdoor industrial corrosion assays was evaluated. The high thickness of the coatings allowed an excellent protection for the three systems studied as long as 2 years of exposure. All epoxy systems imparted protection as barrier coatings, no failure being induced in the films. This behavior is fully consistent with EIS results, which reflected high coating resistances and low coating capacitances. Figure 6 shows the absence of any blistering in epoxy−DMSO/PAni and epoxy−DMSO/PTE after 2 years of exposure, indicating that they represent a good alternative to the less sustainable coating formulated with xylene and zinc anticorrosive additives.

Figure 6. Digital photographs of coated samples exposed to outdoor assays at initial exposure (a) and after 2 years (b), above the brine tank at Solvay Martorell S.A. From left to right: epoxy−DMSO/PTE, epoxy−DMSO/PAni, and epoxy−xylene/Zn.

CONCLUSIONS

Solvent-borne products, which play yet a dominant role in the protective coatings marketplace, are generally preferred to water-borne products; despite the late had an increased share to 15% of market penetration. These preferences are due to considerations such as excellent performance, application and handling characteristics and aesthetic appearance. A key advantage of this work is the ability to make not only a two-component epoxy primers with drastically low VOC value (70 g/L) but also high performance anticorrosive coatings free of toxic inorganic zinc components. The solvent used in the epoxy paint formulation offers less health and environmental hazards than the traditionally used solvents, such as aromatic hydrocarbons and alcohols. Although the epoxy coatings based on DMSO as solvent and PTE or PAni-EB as anticorrosive pigments have extremely slow surface dry due to the nonvolatile component, they have excellent corrosion resistance properties. Moreover, the adhesion to metallic substrates remained for almost 2 years in outdoor corrosive ambient, which makes them useful in marine and heavy duty industrial applications. Furthermore, the resistance protection results provided by epoxy coatings formulated with DMSO are comparable to those achieved with coatings formulated with xylene.

While researchers in industrial settings must be free to choose their own solvent content, inside the maximum VOC limit content value of 290 g/L for multipack primers and intermediates established by European Community in January 01, 2012; those of us who are motivated to reduce solvent-related environmental damage focus our research efforts on potential solutions to those problems. Therefore, the benefits of the present study must be measured against the objective of significantly reducing VOC emissions from the xylene-based epoxy protective primers, usually used outside installations, and to eliminate zinc as an anticorrosive additive for epoxy primers for steel protection.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1, S2, and S3 and Tables 1 and 2. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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