Adhesion enhancement of powder coatings on galvanised steel by addition of organo-modified silica particles

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Abstract

The addition of organo-modified silica particles (OSP) to organic monolayer coatings has been investigated as an alternative to the use of primers or surface pretreatments in galvanised steel substrates. A commercial additive consisting of trifunctional organosilane (alkyl-triethoxysilane) grafted on silica particles was directly incorporated at different concentrations (1, 2.5, 3.5 and 4.5 wt%) as an integral additive in a polyester powder coating. The OSP were characterised physicochemically by means of FTIR and TGA, and the coating formulated by DSC. The anticorrosive properties of the systems were evaluated by means of electrochemical impedance spectroscopy (EIS), showing improvements with all the formulations containing the OSP, especially in the coating with 2.5% OSP. In order to explain this behaviour, morphological (using SEM) and adhesion studies were done. The formation of agglomerates in the powder coatings was detected when the concentration was over 2.5%. There was an improvement in the adhesion of the coating to the substrate for all the samples containing the OSP but especially for that containing 2.5%. The impact resistance was increased too, especially in the formulations with 2.5% and 3.5%.

Keywords:
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1. Introduction

Corrosion protection by powder organic coatings is considered one of the most effective and lasting mechanisms to protect metallic substrates [1,2]. However, effective protection is only possible if the coating stays bonded to the substrate during the design life of the metallic structure. In fact, conventional processes usually require an initial primer or surface pretreatment prior to applying the coating to facilitate adhesion to the substrate. This step implies an increase in the cost of corrosion protection as well as environmental problems because in many cases chromium and other heavy metals are used [3,4].

Organosilane technology emerges in the field of corrosion control of metal as a new and environmentally safer alternative to replace chromate conversion coating [5–9]. Silane adhesion promoters are silicon-based chemicals that contain two types of reactivity – inorganic and organic – in the same molecule. A typical structure is (RO)3Si–(CH2)n–R’, where RO is a hydrolysable alkoxy group (e.g., methoxy, ethoxy and isopropoxy) that can react with various forms of hydroxyl groups present in mineral fillers or polymers and provide linkage with inorganic or organic substrates, and R’ is an organofunctional non-hydrolysable organic moiety group that provides organic compatibility or co-reacts with the coating polymer [10].

In recent years, adhesion promoters based on organosilanes have been used as a metal pretreatment and applied to metallic substrates [11–15]. The formation of thin silane protective films is due to two condensation reactions, one among the silanol molecules themselves (Si OH, hydrolysis products of alkoxy groups), and the other between the silanols and metal hydroxyl (Me OH) substrates to form Si OC3H7 and Si O Me covalent bonds, respectively. Because of the thinness of the resulting film [16], silane films applied alone over a metallic substrate exhibit some limits when long-term protection is required, and a top organic coating to achieve high anti-corrosion performance becomes a necessity [13,17,18].

Further advances in the improvement of corrosion protection using organosilane technology consist of modifications of liquid organic coatings. Zhang et al. developed two ways by which silane monomers were incorporated into epoxy paints; they can be physically mixed with the epoxy coating [19,20] or chemically grafted to the epoxy resin before the coating formulation [21–23]. Van Ooij et al. reported an improvement by incorporating silanes directly on a polyurethane resin system to obtain a ‘superprimer’ with outstanding adhesion and corrosion protection properties [24]. The potential anticorrosive properties of these resin-silane...
combinations are based partly on the improved the adhesion between the coating and the metallic surface (Si—O—Me bonds formed as a result of reactions between silanol groups and metal hydroxyls). However, directly incorporation of silanes in powder coatings has not yet been studied. In this case, organosilane precursors grafted onto inorganic fillers seem to be a possible alternative to achieve a suitable additive for powder systems.

In this work, we assess the effect of using organo-modified silica particles (OSP) as an integral additive in polyester powder monolayer systems for anti-corrosion applications.

2. Experimental

2.1. Materials

The coatings were developed from a saturated carboxylated polyester resin of low molecular weight combined with a N,N,N',N'-Tetrakis(2-hydroxyethyl)-hexanediamide crosslinker in a 95:5 ratio. The composition of the system was 57.7% resin, 3.3% crosslinking agent, 30% titanium dioxide, 4.7% inorganic filler (barite), 3% flow agent, 0.5% levelling agent, 0.3% degassing agent (benzoin), 0.3% polyamide wax and 0.2% Teflon wax.

The silane used in this work was a commercial additive consisting of trifunctional organosilane (alkyl-triethoxysilane) grafted to the surface of amorphous silica particles with specific surface area of 0.8812 m²/g (reference ESQUIUM DL-8302/7, supplied by Esquim S.A., Barcelona). Different concentrations of the additive (OSP) were incorporated into the formulations replacing the inorganic filler (barite) except in the reference formulation. Table 1 summarises the compositions of the samples studied in this work.

2.2. Powder coating formulations/substrate preparation

Powder coatings were premixed and hand-shacked before extrusion in a single screw extruder (Haake Rheomex 254). The extrusion temperature was set to 100 °C, the residence time was approximately 1 min and the torque generated was 20 Nm. After that, the materials were ground in a Moulinex Mill MX843 and sieved through a mesh size of 140 μm. The five different powder coatings were deposited over galvanised steel test panels from Espan color S.L., previously degreased with acetone, by means of an electrostatic gun. All the coated samples were cured at 180 °C for 15 min and the thicknesses obtained were 90 ± 10 μm.

2.3. Testing methods and equipment

2.3.1. Scanning electron microscopy (SEM)

The morphology of the coatings was observed by scanning electron microscopy (LEO 440i SEM) with digital image acquisition. The samples studied were obtained from coatings detached from their substrates after cryofracturing. The back-scattered and secondary electron images were complemented by appropriate chemical information from energy dispersive X-ray (EDS) analysis acquired as point and/or line scans.

2.3.2. Mechanical tests

2.3.2.1. Impact resistance test. Impact testing was performed in accordance with ISO 6272-2:2002. A 1 kg dart mass is dropped down from different heights up to 1 m and impacted at the back of the painted panel, causing its rapid deformation [17,25,26]. The coating’s resistance to impact may be determined from observing the film (cracked or peeled off). Five specimens of each formulation were prepared and tested.

2.3.2.2. Cross-cut test. Paint adhesion was investigated in accordance with ISO 2409:2007, using a cutter with six blades that make square lattice cuts 2 mm wide on the coating film. The cuts were made through the coating film with a steady motion using the minimal sufficient pressure on the knife. The five specimens of each formulation were visually evaluated to detect any delamination of the film. The classification of the delaminated film was based on the criteria and standard stipulated in ISO 2409:2007.

2.3.2.3. Adhesion test. A dry adhesion test was performed in accordance with ISO 4587-2003. The specimen preparation procedure for the adhesion test consisted of depositing coatings with different OSP contents between two rectangular and degreased galvanised steel substrates, as can be seen in Fig. 1 [27], and curing at 180 °C for 30 min. After the curing process, the samples were tested using an Instron Universal Test Machine 4469 H 1907 with a load cell of 50 kN and a crosshead speed of 1 mm/min. Data on load and deformation were registered. Shear stress was obtained by dividing the shear force by the cross-sectional area. Fracture modes were evaluated by means of an optical microscope. Five specimens of each formulation were prepared and tested.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used to determine the glass transition temperature (Tg) of the different cured samples. Scans were performed on a Mettler DSC-821e thermal analyser calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). Samples typically weighing 20 mg were cured in aluminium pans under nitrogen flow at a scan rate of 10 °C/min in the range of −20 to

![Geometry of the lap joint in the adhesion test.](image)
200 °C, cooled down to −20 °C and then heated again to 200 °C at the same heating rate to obtain the \( T_g \) values.

### 2.3.4. FTIR spectroscopy

Fourier transform infrared (FTIR) spectra were collected for the powders using a Jasco FT/IR-6200 spectrometer in attenuated total reflection (ATR) mode. The FTIR-ATR instrument was operated in the wavenumber range of 600–4000 cm\(^{-1}\), with a diamond/ZnSe crystal, 32 scans and resolution of 4 cm\(^{-1}\). A background scan of clean diamond/ZnSe crystal was acquired before scanning the samples.

### 2.3.5. Thermogravimetric analysis (TGA)

In order to determine the influence of the OSP on the thermal stability of the formulations, thermogravimetric tests were carried out using a TG-STDA Mettler Toledo thermogravimetric analyser. Samples of approximately 15–20 mg were scanned from 50 up to 900 °C at 10 K/min. All scans were performed with a flow of 50 cm\(^3\)/min of nitrogen.

### 2.3.6. Electrochemical impedance spectroscopy (EIS)

The effect of adding the OSP on the anticorrosive properties of the formulated powder coatings was evaluated by EIS tests. A three-electrode system was used, in which the sample without coating acts as the working electrode, an Ag/AgCl electrode is the reference electrode and a Pt electrode is the counter-electrode. The area of the painted metal surface was defined by a cylindrical open PVC tube (9.62 cm\(^2\) delimited circular area) that contained an aqueous electrolyte solution (3.5 wt% NaCl). EIS measurements were performed on ZAHNER-IM6ex electrochemical workstation. A sinusoidal AC perturbation of 10 mV amplitude coupled with the open circuit potential was applied to the metal/coating system inside a Faraday cage in order to minimise external interference with the system. The EIS tests were performed in the frequency range from 100 kHz to 10 mHz. All measurements were conducted at room temperature (≈25 °C). The experimental electrochemical data were collected and analysed using the Thales software developed by ZAHNER and the Medco Assay commercial software developed by Medco S.L., respectively.

An equivalent circuit model most widely used by many authors for analyse organic paint systems to protect metals [19,21,28–30], shown in Fig. 2, was employed to analyse the EIS spectra. The circuit consisted of a working electrode (metal substrate), a reference electrode, electrolyte resistance \( R_s \), coating pore resistance \( R_{po} \), coating capacitance \( C_C \), polarisation resistance \( R_p \) and double layer capacitance \( C_{dl} \). Fitting the EIS data to the circuit by means of the Z-view software determined the values of its passive elements, which are generally assumed to be related to the corrosion properties of the system [31]. \( R_{po} \) can be related to porosity and the deterioration of the coating, \( C_C \) to the water absorption by the coating, \( R_p \) to the polarisation resistance of the interface between the coating and the metal substrate and \( C_{dl} \) to the disbonding of the coating and onset of corrosion at the interface [32–34]. To obtain more precise fitting results, constant phase elements CPE (represented here as C) replaced capacitive elements in the equivalent circuit, giving the software values of capacitance in units of \( \varepsilon^4/\Omega \) together with a parameter known as “n” instead of \( \varepsilon/\Omega \) or \( F \) units. The chi-squared parameter of the fit was always less than 0.01.

### 3. Results and discussion

#### 3.1. Characterisation of the organo-modified silica particles (OSP)

Fig. 3a shows a SEM picture of the OSP at 1000 × magnification. It can be seen it is composed of small particles and aggregates with sizes on the scale of tens of microns. EDS analysis of a single particle revealed the presence of carbon in the composition, attached to the organic fraction in the additive, confirming the organo-modification of the silica particles (Fig. 3b).

FTIR spectra of the OSP are presented in Fig. 4. A broad band appears at 3378 cm\(^{-1}\) corresponding to the SiO–H stretching vibration. The alkylic chains in the organo-modifiers in the OSP can be detected by the presence of typical bands at 2950–2930 and 2850 cm\(^{-1}\), attributed to asymmetric and symmetric CH\(_2\) stretching, respectively. Bands corresponding to CH\(_2\) bending vibrations are also detected with low intensity in the 1390–1400 cm\(^{-1}\) range. Detection of these bands confirms that the grafting of the silica particles was carried out predominantly by alkoxysilane-containing alkyl groups as a nonhydrolyzable organic radical. Ethoxy groups from the hydrolysable part of the alkoxysilane molecules should be detected at 1170–1160, 1100 and 1085 cm\(^{-1}\) [35]. However, these bands are masked by the broad, intense peak obtained at 1028 cm\(^{-1}\) that may come from Si O Si connections from the amorphous silica particles, as well as those formed during the silanisation reaction with the alkoxysilane grafted onto them [36].

![Fig. 2. Equivalent circuit used to model EIS impedance data, where passive parameters (Rs, electrolyte resistance; CPEc, constant phase element of the coating capacitance; CPEdl, constant phase element of the double layer capacitance; Rp, polarisation resistance) can be defined.](image-url)
Fig. 4. FTIR spectrum of the OSP.

Fig. 5. TGA (—) and DTGA (----) curves the OSP.

TGA measurements revealed a first slight weight loss around 150 °C due to the ethoxy groups from the alkoxysilane, and a second loss that can be attributed to an oxidative thermal decomposition of non-hydrolysable alkyl chains (Fig. 5). The total weight loss was calculated at around 35%, giving insight into the degree of modification of the silica particles.

3.2. Powder coating morphological characterisation

Micrographs of the coatings containing 0, 2.5 and 4.5% OSP at 2000× magnification obtained by SEM in backscattered electron mode are shown in Fig. 6. All of them show a heterogeneous structure typical of organic powder coatings, in which three predominant phases can be identified. The brightest phase corresponds to barite particles, the darkest one corresponds to resin and the clearest particles are TiO₂ pigment perfectly dispersed in the polyester resin matrix. When the OSP are added to all the formulated systems it cannot be detected in the SEM pictures of the samples until a content of 3.5% is reached. For higher contents of OSP, the additive seems to form agglomerates, which can be above 10 μm. These agglomerates are located close to the surface of the coating (Fig. 6c). This fact may indicate the existence of a critical value (ca. 2.5%) above which the resin cannot retain a greater amount of OSP, hence forming agglomerates that are expelled to the surface, probably during the curing cycle of these paint systems.

The glass transition temperatures (Tg) obtained for the five coatings formulated with different OSP concentrations are shown in Table 1. As can be seen, there are no significant variations between them, indicating that the amount of additive incorporated does not alter the degree of crosslinking in the polyester system.

3.3. Mechanical and adhesion properties of the powder coatings

Fig. 7 shows pictures of the five samples after an impact test from a height of 100 cm with a 1 kg dart. A clear enhancement in the impact resistance compared to the reference coating can be observed with the addition of even small amounts of the OSP. Among all the systems studied, the samples with concentrations of 2.5% OSP presented only minor radial cracking in the area impacted compared with those containing either greater or smaller amounts of additive. The samples with 1% and 4.5% OSP show a fractured surface with a higher degree of delamination.

In the case of the cross-cut test, the edges of the cuts are completely smooth without detachment of flakes for all the samples except the 4.5%, which showed a small delamination in one intersection of the lattice, a defect that is detectable only if it is inspected under a magnifier.

Fig. 6. SEM pictures at 2000× magnifications of coatings detached from the substrate: (a) reference, (b) 2.5% and (c) 4.5%.

Fig. 7. Impact resistance pictures of the formulated coatings: (a) reference, (b) 1%, (c) 2.5%, (d) 3.5% and (e) 4.5%.
The decrease in $\sigma_{\text{shear}}$ when a certain amount of OSP is exceeded can be explained by the presence of agglomerates. This fact can be clearly observed in the SEM image in Fig. 6c. The formation of adhesive agglomerates and their migration to the surface of the coating during the curing process can imply embrittlement of the paint film. Moreover, the poor dispersion may lead to a lower concentration of OSP than should be present in the coating–substrate interface, thus limiting the formation of Si–O–metal covalent bonds.

### 3.4. Electrochemical characterisation

Fig. 10 shows a Bode plot representing the impedance response (impedance modulus and phase angle) versus frequency for coatings formulated with different amounts of OSP after 24 h (Fig. 10a) or 2016 h (Fig. 10b) of exposure to the electrolyte. As can be seen, the coating response during short times of exposure is almost capacitive in all formulations, with almost no difference between them. However, in Fig. 10b, three very clearly differentiated trends can be observed. The first corresponds to those samples without or with just a small amount of the additive (reference 0% and 1%), which show very low impedance values and are almost resistive (phase angle with values near to 0°) in all frequency ranges. The second is represented by the 2.5% coating, whose impedance module gives a straight line at low and medium frequencies, with...
Fig. 11. Evolution of pore resistance $R_{p}$ (a), coating capacitance (b), polarisation resistance $R_{p}$ (c) and double layer capacitance $C_{dl}$ (d) for coatings with different OSP concentrations: 0% (•), 1% ( ), 2.5% ( △ ), 3.5% ( ▽ ) and 4.5% (★) after 2016h of exposure to electrolyte.

The above-described results definitely show that the incorporation of OSP into the formulated systems can improve their corrosion performance, suggesting this improvement achieves an optimum value at around 2.5% by weight of the additive. This enhancement can be related to the replacement of the barite by the organically modified silica particles, which could increase the packaging of the coating leading to a more cohesive network and an improvement of the general paint properties (as can be seen in the electrochemical parameters related to the coating and to the interphase). Moreover, a second mechanism that could explain a better performance of the systems is the adhesion improvement due to the reaction of the residual unreacted hydroxyl groups of the OSP with the hydroxyls groups of metal surface.

4. Conclusions

Use of organo-modified silica particles with silanes (OSP) as an adhesion promoter in a polyester powder coating was studied. The results show that OSP incorporation leads to an improvement in the adhesion properties of the coatings, as well as in their corrosion protection, up to 2.5 wt%. Concentrations beyond 2.5 wt% entail the formation of aggregates, as observed in SEM images, leading to decreases in mechanical and electrochemical performance.

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