Original Article

Performance of ultraviolet exposed epoxy powder coatings functionalized with silica by hot mixing

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ABSTRACT

The effect of hydrophilic nanosilica additions on the (1−3% by wt.) mechanical performance of epoxy powder coatings after UV exposure was investigated in this study. The epoxy coatings were prepared by mixing a commercial epoxy powder with nanoparticles in a hot mixer, an alternative method that is simpler than extrusion. Powders were electrostatically applied on carbon steel and cured to obtain coatings. The epoxy-based coatings were exposed to a xenon lamp with an irradiance of 550 W m⁻² for 500 h. Chemical structure of coatings was characterized before and after xenon exposure, using an attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Glass transition temperature (T_g) was measured with differential scanning calorimetry (DSC). Mechanical and wear tests were performed in order to study the difference among the coatings without and with silica nanoparticles after UV exposure. Surface of the coatings was analyzed with scanning electron microscopy (SEM), as well as the wear tracks to assess the wear mechanism. Finally, aesthetic properties (gloss and color) were also evaluated. The results confirm that the use of SiO₂ nanoparticles in amounts up to 2% allows less chemical and physical degradation of the surfaces and better wear resistance than the plain epoxy coatings after xenon exposure was found for 1% coating.

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1. Introduction

Organic coatings are a widely used method for protecting metals from corrosion, while conferring specific aesthetic attributes. In recent years, the growth of nanotechnology has made it possible to apply novel techniques for the design and development of new functional coatings to create hybrid nanomaterials [1]. Some studies using nanotechnology have focused on the improvement of corrosion resistance [2−4], others on the improvement of mechanical properties and wear resistance [5−7], while others have sought to improve weathering or ultraviolet degradation [8−10]. At the same time, when carrying out this type of strategy, it must first be ensured that the mixing method and the materials used are adequate, since obtaining a heterogeneous material would worsen the final properties of the organic coatings [11,12].

Among the different types of organic coatings, epoxy-based ones are widely used due to their excellent adhesion...
to substrates, superior mechanical and anticorrosive properties and their good thermal resistance [13,14]. Nevertheless, the main disadvantage of epoxy resins is their low resistance to UV light, heat or humidity, which causes degradation of these coatings if they are exposed outdoors [15,16] and limits their durability. An improvement of the reduced weathering resistance of the epoxy powder coating will increase even more their applicability.

Previous studies have been mostly focused on conventional liquid coatings. However, the novelty of this work is the use of powder coatings, due to the advantages that they have over liquid coatings. Some advantages are the lower amount of lost material, the improved mechanical and aesthetic properties, and most importantly, the fact that they are more ecofriendly because they do not contain solvents in their composition [17,18]. Nowadays, these significant advantages of powder coatings have led to their being increasingly used in numerous industrial applications [19].

The main weathering degradation processes that usually affect organic coatings are the photooxidation and hydrolysis reactions. The degradation mechanisms are usually complex, but in general, photooxidation is normally responsible for increasing the crosslinking of the polymer, making it harder and more rigid; whereas hydrolysis reactions result in a chain scission of the polymer [20]. Some of the possible consequences of these processes for the organic coatings are loss of aesthetic and mechanical properties, chalking, or presence of microcracks in their surface [9,21–25]. In any case, the final properties will depend on the combination of both reactions, since they are complex mechanisms.

There are studies related to the effect of SiO$_2$ nanoparticles on the UV durability of different coatings [9,26–30]. The suggested benefits of both hydrophobic and hydrophilic nanoparticles on polyurethane coatings through UV–vis spectral studies [9] were confirmed under UV-B lamps [27]. The chemical degradation of plain polyurethane coating (affecting NCO and alkyl groups) provokes chain scission and carbonyl formation, being this chemical degradation much less pronounced when nanosilica was added [27]. This increased durability against UV light in these coatings has been attributed to the fact that nanosilica absorbs UV radiation [30]. The positive effect of those additions on the gloss of UV exposed polycrylate polyurethane coatings have also been shown [28], while a slight negative effect on the color of UV-A exposed latex films [26] has been reported. The addition to certain epoxy resins do not affect whiteness of UV exposed coatings [29]. In addition, the particle size must also be considered, since the larger the specific surface, the greater the protection against UV [31]. However, no studies have been found on the UV resistance of epoxy powder coatings with nanoparticles, taking into account chemical changes and their effect on mechanical properties and wear resistance.

The addition of SiO$_2$ nanoparticles has been undertaken in this work, because they are a good option for improving mechanical and wear properties of epoxy coatings, both in liquid [3] and powder [32] organic coatings. Moreover, instead of the traditional procedure of extruding for dispersing nanoparticles in a solid plastic matrix, a more economical, innovative procedure was used: hot mixing. The effect of the nanoparticles addition in epoxy powder coatings by this method has already been studied in previous research [33,34], obtaining positive results related to the improvement of the mechanical properties of as-manufactured coatings. However, epoxy coatings are very sensitive to weathering and these improvements could change under irradiation. The main goal of this study is to explore how the addition of silica nanoparticles can affect the degradation that the epoxy powder coating suffers when it is exposed to UV-B radiation, and to know if they can hinder the decrease on the mechanical properties and wear resistance of the coatings. Wear resistance is a key factor in guaranteeing the durability of the barrier properties and corrosion protection of the organic coatings. Although there are some authors who have studied different mechanical properties of organic coatings previously exposed to an UV source [20,21], until now there have been very few wear studies of organic coatings that have been exposed to UV [10], with wear being one of the most frequent cause of damage to the coating. Therefore, it is considered important to study the wear resistance of weathered coatings.

2. Experimental

2.1. Materials and samples preparation

In this study, a commercial epoxy powder coating was used (Cubson International Consulting S.l., Spain) in order to manufacture functionalized organic coatings. The functional groups of the epoxy powder (before curing) were previously analyzed [33], being found oxirane groups to provoke crosslinking. This powder coating also contains pigments (TiO$_2$, 2 wt.%) and additives (talc, 14 wt.%, and dolomite, 24 wt.%), typically found in organic coatings.

As nanoreinforcements, hydrophilic silica nanoparticles (AEROSIL® 90), with a surface area of 75–105 m$^2$ g$^{-1}$ were employed (Evonik, Germany). The diameter of the primary particles is about 20 nm. However, in a previous work [32], it has been checked that this type of SiO$_2$ nanoparticles form aggregates of fine particles. The amounts of silica nanoparticles used were 1, 2 and 3 wt.%. In order to achieve homogeneous coatings, a hot mixer model Haake Rheocord 252p (Thermo Fisher Scientific Inc., USA) was used as the mixing method (in dry conditions). The mixings were carried out at 40 rpm and at 72 ± 1°C for 15 min. This method was previously used with very good results [33,34]. The ability of mechanical means to split the agglomerates and aggregates of commercial nanoparticles has been proved by transmission electron microscopy (TEM) observations [32]. The previous TEM study carried out [32] have not allowed detecting the presence of any of the original aggregates, and only isolated nanoparticles were found. Hence, it can be assumed that the mixing must have caused, at least, partially, a breaking of the aggregates. Of course, the presence of some of the original nanoparticles aggregates cannot be completely discarded after these observations. Anyway, considering the results of previous mechanical studies [32], it can be assumed that their undesirable presence would take place in amount and/or size, which would not be detrimental. Thus, 5 organic coatings were studied and labelled as: AR (as received epoxy powder coating), 0% (the AR passed through
the mixing method), 1%, 2% and 3% (labelled according to the content of nanosilica by wt.%).

Epoxy powder coatings were applied on degreased carbon steel substrates (152 × 76 × 0.8 mm), with a Pulverizadora Manual Easyselect electrostatic spray gun and a control unit OPTITRONIC (ITW GEMA, Switzerland). The voltage source was 100 kV. The curing process was carried out in an oven for 15 min at 180 °C (conditions given by the manufacturer). The thickness of the cured epoxy coatings was about 70 ± 10 μm.

Accelerated weathering of the samples was carried out in a xenon test chamber Solarbox3000 (Cofomegra, Italy). The conditions were: an irradiance of 550 W m⁻² (in the range of 290–800 nm), with an RH of 50%, absence of water immersion and a black panel temperature of 65 °C. Most of the tests to evaluate performance of coatings were carried out after 500 h of exposure, except for the aesthetic properties that were also measured after 250 h.

2.2. Characterization and testing

All organic coatings were analyzed by Fourier transform infrared spectroscopy (FTIR), using a Brucker Tensor 27 spectrometer (Bruker Optik GmbH, Germany) with a Golden Gate attenuated total reflection (ATR) accessory (Specac, UK). ATR-FTIR spectra of the epoxy coatings were recorded in the range of 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹ and 32 scans. At least two scans were performed for each coating and each exposure condition, being sample preparation always the same. As all spectra were taken under the same conditions and in absorbance mode, hydroxyl (Eq. (1)) and carbonyl (Eq. (2)) indexes were calculated with the absorbance intensity (I_{Abs}) of the bands [15,35] in order to quantify and compare (at least in an approximate manner) the xenon degradation of the organic coatings:

$$\text{Hydroxyl index} = \frac{I_{Abs} \text{3394 cm}^{-1}}{I_{Abs} \text{2927 cm}^{-1}} \times 100$$ (1)

$$\text{Carbonyl index} = \frac{I_{Abs} \text{1720 cm}^{-1}}{I_{Abs} \text{2927 cm}^{-1}} \times 100$$ (2)

The glass transition temperature (T_g) of all exposed epoxy coatings was measured with a differential scanning calorimeter (DSC), model 822 (Mettler Toledo GmbH, Switzerland). Aluminum crucibles of 40 μl were used with a sample weight of 5.5 ± 0.2 mg. Nitrogen was used as purge gas (flow of 35 ml min⁻¹). The temperature range was 25–180 °C and the heating rate was 20 °C min⁻¹.

All exposed epoxy coatings were analyzed by scanning electron microscopy (SEM), using Teneo-LoVac (Thermo Fisher Scientific Inc., USA) equipment with a 10 kV electron beam in order to study their surface morphology.

The wettability of all epoxy coatings was examined before and after xenon exposure, through water contact angle measurements. A Dataphysics OCA15 plus goniometer and a SCA20 software (DataPhysics Instruments GmbH, Germany) were employed. At least five measurements were made on each coating.

Mechanical properties such as universal hardness (HU) and plastic work (W_{plast}) of all the epoxy coatings were tested after xenon irradiation with a universal hardness tester ZHU 2.5 (Zwick Roell, Germany). The conditions used were a load application speed of 1 mm min⁻¹, a load removal speed of
10 mm min$^{-1}$ and a load of 5 N. Ten measurements were made on each epoxy-based cured coating after xenon exposure.

Wear tests were performed in order to study the wear resistance of all organic coatings after the xenon exposure. A UMT Tribolab tribometer was used (Bruker Optik GmbH, USA). The tests were performed, under dry conditions, using a load of 5 N, for 10 min and a frequency of 10 Hz. The countermaterial was a stainless steel ball with a diameter of 6 mm. Three tests were made on each sample. The coefficient of friction (COF) was also registered during each wear test. The wear tracks of all materials were studied in an Olympus DSX500 optoelectronic microscope (Olympus Corporation, Japan). The average value of the depth of each wear track was measured, obtaining at least seven values for each wear track. The wear mechanism of the different epoxy coatings was also studied by SEM, using both the circular backscatter detector (CBS) and the Everhart-Thornley detector (ETD).

All mechanical and wear tests were carried out with the same conditions as previous studies \cite{33,34} in order to compare the results to those of non-exposed coatings.

Gloss and color were also analyzed in order to study the possible changes in the aesthetic properties. Gloss measurements were made with a Refo 3 glossmeter (Hach Lange, USA), using 60° (for semigloss surfaces), based on ISO 2813 standard. Color was measured under D65 illuminant, 2° observer and exclusion of the specular component (SCE) on X-Rite Color-Eye® XHT (X-Rite Inc., USA), in accordance to ISO 11664 standard. Both types of measurements were performed before exposure and after 250 h and 500 h of xenon irradiation exposure. At least four measurements were made in each case.

3. Results and discussion

3.1. Physical and chemical characterization

ATR-FTIR spectra were measured and analyzed for all epoxy samples, before and after the xenon lamp exposure, in order to study the possible chemical changes on the epoxy coating.

<table>
<thead>
<tr>
<th>Wavenumbers (cm$^{-1}$)</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>3650–3000</td>
<td>-OH st</td>
</tr>
<tr>
<td>3049</td>
<td>ArC-H st, C–H st oxirane</td>
</tr>
<tr>
<td>2961–2868</td>
<td>-CH$_3$, –CH$_2$- st</td>
</tr>
<tr>
<td>1720–1649</td>
<td>C=O st</td>
</tr>
<tr>
<td>1608,1506</td>
<td>ArC-C</td>
</tr>
<tr>
<td>1455</td>
<td>-CH$_3$ δ as, –CH$_2$- δ</td>
</tr>
<tr>
<td>1298</td>
<td>C–O–C st as, oxirane</td>
</tr>
<tr>
<td>1236</td>
<td>ArC-O-C- al st as</td>
</tr>
<tr>
<td>1179</td>
<td>ArC-H δ ip</td>
</tr>
<tr>
<td>1110</td>
<td>Si–O–Si</td>
</tr>
<tr>
<td>1026</td>
<td>ArC-O-C- al st s</td>
</tr>
<tr>
<td>825</td>
<td>ArC-H δ oop</td>
</tr>
<tr>
<td>729</td>
<td>-CH$_3$ δ, for C–(CH$_2$)$_n$–C n &lt; 4</td>
</tr>
</tbody>
</table>

St: stretching, Ar: aromatic, δ: bending, s: symmetric, as: asymmetric, al: aliphatic, ip: in plane, oop: out of plane bending, n: number of CH$_2$ groups.
surfaces. Spectra corresponding to all coatings under study can be seen in Figs. 1 and 2. Table 1 shows the assignment of each band after the corresponding careful analysis [33,36–39]. Absorbance measurement mode was selected to assure a linear relationship between absorbance and concentration. Hence, in Table 2, the hydroxyl and carbonyl indexes of the organic coatings (according to Figs. 1 and 2) can be seen.

The most important difference observed among the ATR-FTIR spectra of the non-irradiated coatings (Fig. 1) relates to silica nanoparticles. It can be seen that the 1110 cm
−1 band increases its intensity with nanoadditions, confirming a correct incorporation of SiO2 in the epoxy coatings [28]. Moreover, the complete disappearance of the epoxide band (oxirane ring present in the raw epoxy powders [33]) at 916 cm
−1 [40,41] indicates a complete curing process of the epoxy resin for all coatings. In addition, the small band at approximately 3650 cm
−1 is somewhat larger in nanoreinforced coatings (Fig. 1). This may be related to the fact that hydrophilic silica nanoparticles contain silanol groups (Si–OH) in their particle surface [42].

Regarding the ATR-FTIR spectra of the exposed epoxy coatings (Fig. 2), certain changes can be observed with regard to the non-exposed coatings. The hydroxyl band (centered around 3394 cm
−1) and the bands in the 1720-1649 cm
−1 range (corresponding to the carbonyl groups) increase after xenon exposure (compared to Fig. 1). The quantification of these changes is found in Table 2, where the hydroxyl and carbonyl indexes were calculated.

Previous studies have shown that the hydroxyl and carbonyl groups could be generated after UV exposure because of the hydrolysis and photooxidation reactions, respectively, which occur after the chain scission and hydrogen abstraction from the polymer backbone [15,25]. Gheno et al. [43] verified that both phenomena can occur at the same time on polyester thermosetting powder coatings. On one hand, the carbonyl index is greater than the hydroxyl index, so the most predominant reaction in these coatings is photooxidation. It is well known that photooxidation starts in methyl groups [25]. The comparison between Figs. 1 and 2 shows the reduction of the methyl bands, especially the one located at 2960 cm
−1, confirming the degradation process of epoxy resin. In addition, the carbonyl index of the reinforced coatings after xenon exposure decreases to some extent, relatively, about 10–15%, compared to the epoxy coatings without nanoparticles (Table 2). Thus, photooxidation would be higher in AR and 0% coatings, which would mean that silica nanoparticles are able to reduce this reaction when exposing the coatings to a UV source, which could be related to increased absorption of UV radiation [27]. It has also been suggested that the protection against UV degradation offered by nanoparticles is due to the fact that they protect the matrix by absorbing UV photons and converting them into heat [44] or scattering UV rays [45]. On the other hand, it can be seen that hydroxyl indexes are similar for all epoxy coatings, except 3%, which has an index at least 25% (for the measurement conditions used in this research) higher than other coatings. Those hydroxyl groups are generated by degradative oxidation reactions, even during carbonyl formation [15,27]. This means that there would be practically no differences in the hydrolysis of the coatings, except for the 3% that would suffer greater hydrolysis than the other epoxy coatings. The high crosslinking achieved for the 3% during its manufacturing [33] can be responsible, at least partially, for the higher number of hydroxyl forming reactions observed in the surface of the coating, as higher chain scission could be expected.

Therefore, the results obtained by ATR-FTIR indicate that the incorporation of silica nanoparticles (up to 2% by wt.) in an epoxy powder coating can lead to better UV performance.

In Fig. 3, results from thermal analysis of coatings are presented. In Fig. 3a, examples of DSC curves are shown. The DSC curves of the coatings before and after xenon exposure show no meaningful transformation but that related to Tg, marked with rectangles, showing a sharp increase of heat flow

| Table 2 – Hydroxyl and carbonyl indexes (%) of all exposed epoxy coatings. |
|---------------------------|---------------------------|
|                         | Hydroxyl index (%)        | Carbonyl index (%)        |
|                         | Before exposure | After exposure | Before exposure | After exposure |
| AR                       | 43.4 ± 0.0      | 64.9 ± 4.3     | 26.2 ± 4.1      | 95.2 ± 4.1     |
| 0%                       | 40.9 ± 0.7      | 64.0 ± 0.6     | 24.4 ± 2.7      | 92.4 ± 2.6     |
| 1%                       | 44.2 ± 1.2      | 65.6 ± 3.3     | 29.3 ± 0.9      | 80.8 ± 7.7     |
| 2%                       | 45.0 ± 2.1      | 61.4 ± 8.7     | 32.0 ± 2.3      | 79.9 ± 9.0     |
| 3%                       | 45.8 ± 1.4      | 83.0 ± 1.2     | 30.1 ± 6.1      | 85.7 ± 3.6     |

![Fig. 3 – a) DSC of some selected non-exposed and exposed coatings; b) Tg value (°C) of all epoxy coatings after exposure, and the increase with respect to the non-exposed coatings.](image-url)
with temperature. Curves clearly show that $T_g$ of the exposed coatings shifts to higher temperatures, occurring this phenomenon in all coatings. All quantified $T_g$ values are presented in Fig. 3b, including the $T_g$ data of all epoxy coatings after 500 h of xenon exposure and the difference with respect to the non-exposed coatings (dif 0 h).

Before the xenon exposure, all $T_g$ values of all the epoxy coatings were around 99 °C so it could be concluded that they were not affected by the addition of SiO$_2$ [33]. Then, it can be seen that the $T_g$ increases for all coatings after the accelerated xenon exposure, especially for the non-reinforced ones (AR and 0%). In addition, the final $T_g$ value after the exposure is greater in the case of the AR and 0% organic coatings. The chemical changes during xenon exposure evaluated with FTIR (Fig. 2, Table 2) explain the increase of $T_g$. When a thermoset material is exposed to UV light, either a decrease in crosslinking due to hydrolysis [15] or an increase in crosslinking due to a photooxidation [43,46] may occur. The increase of $T_g$ found (Fig. 3) is consistent with a more marked increase in the carbonyl index with exposure (Table 2) than that observed in the hydroxyl index. This fact suggests that the degradation phenomena could make the polymer structure more rigid,
since carbonyl groups would be responsible for a greater difficulty of movement for the polymer chains, decreasing their ability to relax stresses, although crosslinking has not taken place.

3.2. Morphological and surface characterization

Figs. 4 and 5 show SEM images of the epoxy coatings after xenon exposure. The darkest zone corresponds to the epoxy matrix, while the small white particles are TiO₂ (typical powder coating pigment), and the big white particles correspond to typical fillers such as dolomite and talc, as previously identified by EDS analysis [33,34].

Non-exposed functionalized epoxy coatings were studied in previous work [33,34], and no type of irregularity or microcracking was observed on them. However, once the epoxy coatings were exposed, microcracks appear all over the coatings surface, indicated by red arrows in Fig. 4. These microcracks can be clearly observed for all coating compositions under study. These microcracks are a result of UV exposure [47], and they are more abundant in the coating with 3% nanoparticles and highly noticeable for the materials without nanoreinforcements (AR y 0%). Increasing the magnifications (Fig. 5) also shows that 1% and 2% coatings only show very few, narrow cracks. Moreover, it seems that cracks are wider in 3% than in the rest of coatings. These results are in agreement with those in Figs. 2 and 3, and Table 2. A greater increase in Tₙ in epoxy coatings without nanoparticles, due to a predominance of photooxidation degradation, has been observed, making the material more brittle and rigid, and causes the coating to absorb stresses, generating these microcracks [22,48]. The 1% and 2% coatings (Figs. 4 and 5) seem to be able to better release structural and thermal stresses, maybe because there is less photodegradation and the Tₙ value increases by a smaller amount. On the other hand, the heavily cracked surface of the 3% coating (Figs. 4 and 5) is also probably due to an increase in the hydrolysis phenomenon, since the carbonyl indexes are similar to those determined for the 1% and 2% epoxy coatings (Fig. 2 and Table 2).

The water contact angle (CA) of all epoxy coatings was also measured in order to complement the study of the structural

Fig. 5 – SEM images of epoxy coatings after xenon exposure, showing cracking at higher magnification.
changes. Fig. 6 shows all CA before and after xenon exposure. All organic coatings had initially similar CA (around 80°) and the addition of hydrophilic silica nanoparticles did not appear to modify the wettability of the non-exposed surfaces. Xenon exposure has considerably reduced CA in all cases, making surfaces more wettable, which suggests a decrease in the protective abilities of the organic coatings. Epoxy coatings (from AR to 2%) after xenon exposure show a similar hydrophilic surface (a CA between approximately 28° and 35°) while 3% epoxy coating has shown a smaller reduction of CA than the rest of the coatings (with a CA of around 60°).

The results obtained for all exposed coatings suggest the creation of new polar groups in all the epoxy coatings after the aging exposition [31,49]. The results obtained in ATR-FTIR (Figs. 1 and 2 and Table 2), proving the occurrence of hydrolysis and photodegradation reactions during xenon exposure in all organic coatings, imply the formation of polar groups, so this decrease in all CA can be easily understood.

The degradation reactions do not explain the smallest reduction of the CA for the 3% epoxy coating. Zahiri et al. [50] tried to explain this anomalous behavior of increasing the contact angle, showing that the decrease in contact angles with increasing solid—liquid interfacial areas is not always valid, as generally predicted by the Wenzel and the Cassie-Baxter models (as found in Fig. 6, in their case related to increased roughening). Both models (Wenzel and Cassie-Baxter) consider that the contact angle is a function of the solid—liquid interfacial area under the droplet. Irregular roughness features can escape from those models. In this research, cracks in the surface of the 3% epoxy coating (Figs. 4 and 5) could modify the expected behavior (Wenzel model). Contact angle behavior is determined by interactions of the liquid and the solid at the so-called three-phase contact line [51], being the interactions at the three-phase contact line those controlling the wettability of heterogeneous surfaces [52]. The equilibrium contact angle should be related directly to the line of least possible mean work of adhesion that the three-phase junction can assume [53]. Those researches focus on asperities and roughness phenomena, although the effect of cracks is suggested. Cracks on 3% coating might provoke an effect of pinning and the presence of the partial slip-condition along the rough surfaces on the liquid, being the change in wettability of this coating dependent on roughness and the geometric shape of cracks, as found in [54]. Moreover, it has also been suggested that special geometrical microstructures, together with trapped air in the closed structures, as can happen in found cracks, whose geometry has not been studied, may lead even to superhydrophobic properties on a hydrophilic surface [55], although just a decrease of hydrophilicity can take place, as shown in Fig. 6.

3.3. Mechanical properties and wear tests

Fig. 7 shows the values corresponding to two different mechanical parameters: the HU (a) and the $W_{\text{plast}}$ (b) of each epoxy coating after the 500 h of xenon exposure and the difference at 0 h of the two properties.

Regarding the HU (Fig. 7a), similar values for all exposed epoxy coatings can be observed, although it seems that the 2% and 3% coatings are slightly harder compared to the other ones. On the other hand, meaningful changes in hardness are observed with respect to the non-exposed coatings. The AR and the 0% coatings have increased the hardness value after exposure, around 40–45 N mm$^{-2}$. Nevertheless, the 1% and 2% nanoreinforced epoxy coatings have increased this value very little (18 N mm$^{-2}$ in the 1% coating and 10 N mm$^{-2}$ in the 2% coating approximately), and the hardness of the 3% epoxy coating has decreased (35 N mm$^{-2}$ approximately). Nanosilica, in the non-exposed coatings, promoted a strong hardening in the resin [34], immobilizing polymeric chains and
increasing the crosslinking of the polymer [6,56,57] and the hardness of the matrix around the particles. This was possible due to the good homogeneity obtained for the dispersion of the nanoparticles in polymeric matrix [58]. Before irradiation, it was observed that the addition of such a high amount of nanoparticles as 3% to the epoxy coatings caused a dramatic increase on the mechanical properties [33,34]. This result can seem excellent, but very hardened materials are unavoidably prone to fragile failure.

After the xenon exposure, the combination of the hydrolysis and photooxidation reactions during the exposure gives rise to different changes in the organic coatings. Photooxidation, increasing the amount of carbonyl groups (Table 2), has an important effect on $T_g$ (Fig. 3) [43], making difficult the movement of polymer chains, and strongly affecting the hardness (Fig. 7) of the plain, unreinforced epoxy coatings. The formation of carbonyls is smaller in 1% and 2% coatings, and the effects on hardness are reduced (Fig. 7), especially taking into account that the composite coatings presented higher hardness values than non-reinforced ones before exposure [34]. While the increase in hardness for 1% coating is barely meaningful, that for the 2% coating is lower, inside the experimental error range (Fig. 7). The irradiation seems to affect to a less extent not only the surface (Figs. 4 and 5) but also the mechanical characteristics of the bulk of these two coatings (hardness indenter deeps into the material approximately from 22 to 25 μm).

Nevertheless, hydrolysis is also present during the UV exposure (Table 2), with its effect being strongly noticeable for the previously most hardened 3% coating (Table 2). Hydrolysis also causes chain scission and, macroscopically, a very marked decrease in hardness is found (Fig. 7). In addition, it cannot be discarded that the formation of cracks, especially when they are bigger (Figs. 4 and 5), might influence the loss of mechanical properties [59], as they are a consequence of stress relief processes of the structure.

The $W_{\text{plast}}$ (Fig. 7b) is related to the ductility of the material. Although similar values can be observed among all exposed epoxy coatings, this property has decreased with respect to the non-exposed coatings. The coatings showing the strongest increase in hardness (Fig. 7a) are those with the most significant reductions in $W_{\text{plast}}$ (0.005 N·mm approximately for AR and 0%). This confirms that the xenon exposure of the coatings makes the coatings less plastic, as a consequence of chemical changes (Figs. 1 and 2, Table 2) affecting $T_g$ (Fig. 3) and hardness (Fig. 7a).

As a general conclusion after analyzing the different mechanical properties of the organic coatings, there are two main observations: on the one hand, coatings without nano-reinforcements seem to become more brittle, as they have greater hardness and less plasticity (which coincides with the fact that they present the highest carbonyl indexes -Table 2-), and on the other, coatings with a high amount of silica (3%) suffer more intense chain scissoring, losing dramatically mechanical properties during irradiation. However, as the initial hardness caused by the nanosilica also determines the final performance, it is important to stress that coatings with 3% nanoadditions are still the hardest ones after xenon exposure, and, in no case, the mechanical properties of reinforced coatings are worse than those of the AR or the 0% after irradiation.

Regarding the information given by the wear tests, all the results are summarized in Figs. from 8 to 11. During the wear tests, the COF values were recorded continuously during the 10 min of the test (Fig. 8). The COF curves of the 2% are very similar to that of 1% (inside the experimental dispersion range), while the 0% are similar to those of the AR.

The evolution of COF presents three different stages in all cases [32,34]. The first stage corresponds to a low and constant COF due to a sliding condition. The second stage corresponds to a gradual increase in the COF in a generally short period of time, which occurs when the wear of the material begins. Finally, the third stage, with a higher and constant COF,
corresponds to pure wear until the end of the wear test. Those phenomena have been previously discussed in depth for non-exposed coatings [34]. However, the shorter first stage on exposed coatings (Fig. 8) compared to non-exposed ones is noticeable [34]. The defects on the surface of exposed materials (Figs. 4 and 5) are probably related to this shortening of the two first stages, related to the nucleation and formation of the wear track. It is important to underline that the wear track starts easily—at shorter times—for the most cracked, the 3% coating, even although is the hardest one. On the other hand, the 1% and 2% present the longest first and second stages, which is compatible with less deteriorated surfaces (Table 2 and Figs. 4 and 5). Hence, a beneficial effect of nanosilica additions in amounts of about 1 and 2% against wear conditions can be drawn from these results. It should also be noted that the final COF are similar for all the irradiated coatings (almost 0.8) and higher than those determined for the coatings before xenon exposure [34]. It must be borne in mind that the differences observed in Fig. 8 regarding the first stages of the wear process are reduced due to the aggressivity of the test, but they could exert a possible eventual noticeable influence under less aggressive conditions.

Fig. 9 shows some examples of wear tracks after xenon exposure of three epoxy coatings: AR, 1% and 3%. The green-yellow part would correspond to the intact coating, while the blue-violet areas correspond to the wear tracks. Therefore, the difference among the coatings with and without silica is clear, with the non-reinforced ones showing deeper wear tracks.

The depths of the wear tracks have been quantified (Fig. 10). Exposed epoxy coatings with silica nanoparticles are more wear resistant, having a depth of 10–15 μm less than the plain coatings, although no differences can be found as the amount of nanoparticles increases. The final depth is the result of the changes occurring in the outer surface, which determines the length of the sliding stage, and those taking place in the bulk coating and affecting their mechanical properties. For the irradiated coatings, the hardness is quite similar, but perhaps slightly higher for 2% and 3% (Fig. 7a). However, the presence of surface cracks (Figs. 4 and 5) can negatively affect the wear behavior. As the 3% is the most cracked, this aspect can partly balance its higher hardness.

The minor increase observed for the hardness of the 2% coating is clearly inside the range of the experimental error (Fig. 7a), and that observed for 1% coating is barely meaningful, while for the other studied coatings start to be relevant. Hence, for 1% and 2% coatings, when the characteristics of the bulk coating are measured, it can be assumed that only minor changes—or very balanced form a mechanical point of view—must have taken place. Most of the chemical and physical degradation on 1% and 2% should have focused on the outer surface of these coatings. Their results are different from those shown for the other three coatings under study.

Moreover, for materials under study, there are meaningful differences among the length of the sliding step before [34] and after irradiation (Fig. 8) that can help to understand some results in Fig. 10. For AR and 0% coatings the sliding steps lasts about 0.5 min, and for 1% about 1 min, that is to say, their
sliding steps are reduced by the chemical degradation of the surface, but in an amount that can hardly be meaningful for the final results.

On the other hand, for the hardest materials before irradiation (2% and 3% coatings), the change in the length of the sliding step is decisive. Before irradiation, the sliding step lasts 4 min for the 2% coating, while this step lasts the whole length of the test for the 3% coating (its hardness avoids the formation of a wear track). The shortening of the sliding stage of 2% coating after irradiation must be related to slightly cracked (Figs. 4 and 5) and chemically degraded (Table 2) surface. These damages favor the onset of the formation of the wear track and explain the increase in its depth (Fig. 10), in spite of the non-noticeable change in the hardness of the bulk material caused by irradiation (Fig. 7a). For the 3% coating, the deeper wear tracks when compared to the non-irradiated coating can also be related to the surface damage (Figs. 4 and 5) and with the decrease on hardness (Fig. 7a) that takes place during irradiation.

Moreover, it is interesting to stress that 1% is the single coating under study that has reduced the depth of the track under the studied conditions. The minor degradation has made initial stage does not change meaningfully. Hence, the slight increase of hardness (Fig. 7a) exerts a positive effect on the wear resistance, being the only material that improves its wear performance after irradiation.

The wear tracks of all exposed epoxy coatings were analyzed by SEM in order to study the wear mechanism in each case. In Fig. 11, it can be observed, as an example, the wear tracks of the AR, 1% and the 3% coatings after the xenon exposure. The wear mechanism of unexposed coatings was explained in detail in a previous work [34].

Different abrasive wear mechanisms can be observed and microcracks transverse to the sliding direction can be seen in SEM images of the wear tracks. For coatings without nanosilica (Fig. 11a and b), a different morphology is observed for the detachment, with smoother surfaces at the bottom of the worn areas. The presence of nanoparticles hinders the material removal under wear stresses, and it takes place with a more irregular morphology for the 1% (Fig. 11c and d) and 2% coatings. Moreover, for the 3% the detachments are reduced in size but much more numerous (Fig. 11e and f).

3.4. Aesthetic properties

To evaluate the aesthetic properties, the non-exposed epoxy coatings were compared, as well as the coatings exposed to the xenon lamp, in this case after 250 h and 500 h.

In Fig. 12, the gloss obtained for each organic coating is shown. The non-exposed, plain epoxy coatings (AR and 0%) show a high initial gloss, while this gloss gradually decreases with the amount of added silica nanoparticles. These decreases in the gloss due to nanosilica have already been reported by other authors [28,60] and are usually related to microstructural or textural changes in the coating surface [23].

Once the coatings have been exposed to UV light, they gradually lose gloss with the exposure. At 250 h, it is observed how the gloss decreases, especially in those coatings that had a highly glossy surface. After 500 h, the decrease of gloss leaves almost matte coatings. This loss of gloss due to ultraviolet exposure is very common. Nanoparticles are not able to improve gloss loss of epoxy coatings, although in other cases, SiO2 nanoparticles can positively affect [28].

Additionally, a study of the color differences of the organic coatings was carried out before and after the xenon exposure. Fig. 13 shows the color variations (ΔE). Again, measurements were also made at both 250 h and 500 h.

Regarding the differences among the non-exposed organic coatings, compared to AR coating (0 h data in Fig. 13), there are practically no differences among coatings, since ΔE shows small values (about 1). In the case of the 3% epoxy coating, the ΔE is somewhat larger than the rest of the organic coatings (around 2). ΔE values lower than 10 are acceptable, as was
Fig. 11 – Wear mechanism of epoxy coatings after xenon exposure: AR (a and b), 1% (c and d) and 3% (e and f).

Fig. 12 – Gloss measurements of all epoxy coatings at different times of xenon exposure (0 h, 250 h and 500 h).
assumed in previous studies [61]. Therefore, it seems that the addition of SiO2 nanoparticles does not influence the color of the non-exposed epoxy coatings, as is found in polyester powder coatings [60].

Once the epoxy coatings have been exposed to the xenon lamp, a larger ΔE value is observed (values shown compare each coating with its non-exposed color). At 250 h, the ΔE is around 5–6, while at 500 h it is around 8–9. The coatings with silica nanoparticles have a slightly greater change in the ΔE than plain epoxy coatings, although the ΔE value of 10 is not exceeded in any case, so these changes can be considered acceptable. Moreover, those ΔE changes are smaller than those found in other coatings [8,26]. This loss of color in coatings exposed to UV light is usually related to photodegradation of the polymer [62].

Furthermore, in Table 3, all the parameters that define the color (L*, a*, b*) of each coating are collected at each exposure time. The L* parameter corresponds with colors ranging from white (+) to black (−), the a* parameter from red (+) to green (−) and the b* parameter from yellow (+) to blue (−).

As can be observed, b* increases (becomes less negative), indicating a yellowing trend in all organic coatings after the exposure, as found in other studies [25,27,63]. Moreover, the change of parameter b* is slightly bigger for the epoxy coatings without nanoparticles (AR and 0%), therefore silica nanoparticles withstand better the typical yellowing of epoxy coatings after UV exposure. However, they become slightly greener (decrease of a*) than non-reinforced coatings.

Moreover, another important aesthetic issue during weathering of coatings is chalking (or chalk resistance). Although it has been seen in some epoxy resins [16,64], it has not been observed for the studied epoxy powder coatings. Though further corrosion tests would be of interest in order to draw definitive conclusions about the protective properties of nanosilica reinforced epoxy powder coatings, the results obtained in this research reveal how SiO2 nanoparticles (in amounts up to 2%) improve the UV resistance of epoxy powder coatings, as well as reduce the surface cracking and the wear damage. In this way, thanks to these improved properties, the service life of these epoxy coatings could probably be longer under weathering conditions. However, for continuous outdoor exposures -clearly unadjusted for epoxy based coatings-, it cannot be discarded that small amounts of nanosilica additions can start to favor hydrolysis reactions and surface cracks if heavy irradiations provokes an intense hardening. As this possibility has not been explored yet, the obtained results would only made advisable this type of functionalized coatings for applications submitted to wear stresses and occasional UV exposure (with a maximum of 1% or 2% of nanosilica).

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**Table 3 – Color parameters of all epoxy coatings at different times of xenon exposure (0 h, 250 h and 500 h).**

<table>
<thead>
<tr>
<th></th>
<th>0 h</th>
<th>250 h</th>
<th>500 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>a*</td>
<td>b*</td>
<td>L*</td>
</tr>
<tr>
<td>AR</td>
<td>38.1</td>
<td>−5.0</td>
<td>−29.7</td>
</tr>
<tr>
<td>0%</td>
<td>37.2</td>
<td>−5.5</td>
<td>−30.5</td>
</tr>
<tr>
<td>1%</td>
<td>37.4</td>
<td>−5.5</td>
<td>−30.5</td>
</tr>
<tr>
<td>2%</td>
<td>37.3</td>
<td>−5.5</td>
<td>−30.5</td>
</tr>
<tr>
<td>3%</td>
<td>36.8</td>
<td>−5.9</td>
<td>−30.7</td>
</tr>
</tbody>
</table>

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**Fig. 13 – ΔE measurements of all epoxy coatings at different times of xenon exposure. The 0 h compares non-exposed coatings to AR. 250 h and 500 h compares each coating with its non-exposed color.**
4. Conclusions

The results obtained in the current study allow to conclude that the addition of silica nanoparticles, in amount of 1% by wt. using hot mixing, is able to delay the degradation process of epoxy powder coatings under UV radiation, making them more wear resistant than plain epoxy coatings. Coatings with 2% of nanosilica, which showed better properties than 1% before irradiation, have also shown a very slight decrease on their mechanical properties after UV exposure. Therefore, it is interesting this type of functionalization for the epoxy powder coatings to increase their durability. Moreover, other interesting conclusions can be drawn from the results obtained during the present study:

- ATR-FTIR results prove that UV exposure provokes degradation though hydrolysis and photodegradation reactions. Coatings with nanoparticles show smaller photodegradation than non-reinforced coatings. Hydrolysis processes are similar among coatings except for 3% coatings, where it occurs at higher extent.
- Surface cracking on the coatings takes place, with coatings containing 1% and 2% SiO₂ having the best performance (fewer cracks).
- Epoxy coatings with 1% and 2% SiO₂ only slightly change their hardness due to UV exposure, while those with 3% suffer a marked decrease in this parameter. As for coatings without nanoparticles, they strongly harden because of the increase in T_g due to greater photodegradation.
- Wear performance depends on the effect of both hardness and surface cracking. Coatings with silica nanoparticles present the best wear behavior (less deep wear tracks).
- Regarding aesthetic properties, the presence of silica nanoparticles does not exert any beneficial effect. The color has acceptable variations after exposure in all organic coatings.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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