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SiO_2 nanoparticle/Polymer composite as anticorrosive coating for A-36 steel

Nanopartículas de SiO_2/compuesto de polímero como revestimiento anticorrosivo para el acero A-36

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Abstract

Automotive paint is used on the surface of automobiles to decorate or beautify the vehicle. However, one of its main purposes is to prevent metal corrosion. Therefore, in this paper, the anticorrosive properties of an epoxy resin-based primer with silica nanoparticles (SPN) are investigated. The coatings were deposited on A-36 steel plates and their efficiency as anticorrosive coatings as well as their adhesion, hardness, finish, and durability properties were evaluated under accelerated aging tests simulating humid and hot weathering conditions.

Corrosion, Anticorrosive coatings, Silica nanoparticles, A-36 Steel, NPS/Polymer composite

Resumen

La pintura automotriz es aquella usada en la superficie de los automóviles, esto para decorar o embellecer el vehículo. Sin embargo, una de sus principales funciones es prevenir la corrosión del metal. En este trabajo se investigaron las propiedades anticorrosivas de un primer a base de resina epóxica con nano partículas de sílice (NPS). Los recubrimientos se depositaron en placas de acero A-36 y se evaluó su eficiencia como protectores anticorrosivos, así como propiedades tales como: adherencia, dureza, acabado y durabilidad ante pruebas de envejecimiento acelerado simulando condiciones de intemperie de humedad y calor.

Corrosión, Recubrimiento anticorrosivo, Nanopartículas de sílice, acero A-36, Polímero compuesto NPSs

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Introduction

Automotive paint is used on the surface of automobiles. It is usually thought that such paint is to decorate the vehicle to make it more attractive to the eye, however, that is not the main function since paint is to prevent corrosion or rusting of the metal (Grtzl T, 2019; Groysman A, 2010).

Corrosion is defined as the degradation of metals due to environmental factors such as humidity and acidic or alkaline conditions of the environment to which the metal is exposed. Corrosive agents are those that cause the metal in its basal state to lose electrons to increase its oxidation state, through the reaction shown in Eq. 1.

$$M \rightarrow M^{n+} + n\ e- \quad (1)$$

Corrosion is a physicochemical phenomenon that causes the degradation of the metal due to the formation of a galvanic cell; as shown in Figure 1a. The metal oxidizes losing electrons and with agents of the medium such as oxygen form the metal oxide (see Figure 1b) that causes the loss of the material causing the decrease of its mechanical properties (Salazar-Hernandez, 2015).

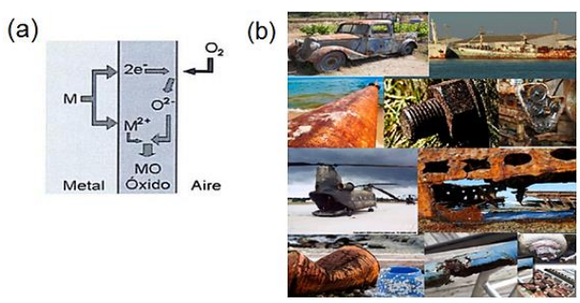

Figure 1 (a) Galvanic cell during corrosion (b) Example of materials with several corrosion

To prevent corrosion in metallic materials there are different alternatives, among them are anticorrosive coatings (Bierwagen G, 2010; Danaee I, 2014; Yi-Chia H, 2014; Wei T, 2005). Today, nanocomposites have been proposed; these are materials formed by the dispersion of inorganic particles with size or structure in the nanometer range in an organic phase, such as polymeric matrices (Zou H, 2008; Percy M.J, 2000; Yang F, 2006; Hung W.I, 2011). The inorganic particles give the material properties such as stiffness and thermal stability; while the polymeric matrix generally retains its flexibility, ductility and processability.

Among the inorganic phases that have been added to polymeric matrices for reinforcement are nanotubes, silicates (montrolite, saponite), metal nanoparticles (Ag, Au), metal oxides (TiO2, Al2O3, SiO2), semiconductors (PbS, CdS) (Zou H, 2008; Mahon J.R, 2022), grafted polymer with □-zirconium (Zhu Z, 2022). Being silicon dioxide (SiO2) one of the additives that have a greater importance due to the characteristics of silica (it is inert, with high thermal and mechanical stability), thus polymer/silica nanocomposites have a wide range of applications ranging from the formation of anticorrosive coatings (Honarvar Nazari M, 2016; Dave P, 2022), reinforcement in mechanical properties (LeBaron P.C, 1999), flame retardants (Kiliaris P, 2010) and biomaterials (Arcos D, 2010).

This paper presents the evaluation of the effect of the addition of silica nanoparticles to a commercial epoxy resin and determine the change in physical properties as well as its ability to act as a corrosion retardant on A-36 steel substrates.

Methodology

NPS/Polymer formulation

Table 1 shows the different formulation conditions performed for this research. The two main components in the formulations are epoxy resin (EP-2000) industrial grade catalyzed with ED-200 (industrial grade) and Aerosil-200 fumed silica (Aldrich, reagent grade). The amounts of silica nanoparticles in the polymer resin vary from 0.5 wt% to 10 wt.%. Two types of mixing were tested to obtain the coatings: magnetic stirring and ultrasound. On the other hand, formulations were obtained without solvent and adding acetone as solvent to improve particle dispersion in the resin.

The composites are applied on A-36 steel surfaces. Before applying the formulations, the metal surface is subjected to a pretreatment that consists of sanding the surface of the specimen with abrasive paper number 400 and washing with water and ethanol using an ultrasonic bath and finally drying the samples at a temperature of 50 ºC for 2 h.

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The coating is applied to the A-36 steel surface treated by immersion, which consists of introducing the metal sample into the solution containing the polymer/silica mixture and then leaving it to dry at a temperature of 50 ºC for 24 h, leaving the sheet in a vertical position.

	Epoxy Resin	NPS	Catalyst	Magnetic mixed	Ultrasound mixed	Without Ketone	With Ketone
0.5NPS/EP-A	10	0.05	1	X		Dispersion	Dispersion
0.5NPS/EP-B	10	0.05	1		X	Dispersion	Dispersion
3NPS/EP-A	10	0.3	1	X		Without Dispersion	Dispersion
3NPS/EP-B	10	0.3	1		X	Without Dispersion	Without Dispersion
5NPS/EP-A	10	0.5	1	X		Without Dispersion	Dispersion
5NPS/EP-B	10	0.5	1		X	Without Dispersion	Without Dispersion
10NPS/EP-A	10	1	1	X		Without Dispersion	Dispersion
10NPS/EP-B	10	1	1		X	Without Dispersion	Without Dispersion

Table 1 NPS/EP composites formulation

Coating characterization

Infrared Spectroscopy (IR-ATR)

Infrared spectroscopy (IR-TF) was used to chemically characterize the coatings. This technique was used to identify the main coating compounds. The spectra were obtained through an ATR-TF Nicolet–iS10 spectrometer, obtaining the average of 16 scans and a resolution of 4 cm–1 with a spectral window of 4000 to 600 cm–1.

Viscosity measurement

The dissolution viscosity was measured using a Brookfield DV2RLV viscometer with UL adapter and TC-650 re-circulator controlling the measurement temperature at 25ºC.

Adherence measurement: Pull of Test

Adhesion tests were performed using PosiTest AT-A equipment. This equipment evaluates the adhesion of a coating based on the critical tensile strength recorded at the time the coating peels off the substrate; the equipment design and test are based on ASTM D4541, D7234 and ISO 4624.

Dispersion of Nanoparticles in the Polymeric Matrix

The dispersion of silica nanoparticles is observed by scanning electron microscopy using a JOEL-6510 plus Scanning Electron Microscope (SEM). In the equipment, the samples are placed on a graphite ribbon without coating of gold to be observable at 500X.

Galvanic corrosion test by gravimetric method

Corrosion tests were performed in accordance with ASTM-B117, using a simulated saline environment with NaCl at 5% by weight as the corrosive agent. A-36 steel specimens with and without coatings were exposed to the corrosive medium using the DIT-105 Peaktech corrosion test bench. The specimens were exposed to a constant current of 0.5A for 90 minutes. At the end of this period, the mass loss caused by corrosion was recorded and the corrosion rate was determined using Eq. 2.

$$V_c = \frac{\Delta m}{A*t}[=]\frac{kg}{m^2 \cdot s} \quad (2)$$

Results

Effect of particle concentration on the viscosity and distribution of NPS on the polymer matrix

Figure 2 shows the effect of the concentration of silica nanoparticles against the viscosity of the formulation, without addition of acetone the observed behavior was exponential, thus the addition of 0.5% of particles increases the viscosity of the resin by 36%; while the addition of 3% of particles increases the viscosity by 541%. Therefore, without solvent, adding these percentages of additive generates slurries difficult to apply and spread on the metal surface. Thus, formulations with nanoparticles containing percentages equal to or higher than 3% are impossible to apply on the substrate to form a thin and homogeneous layer.

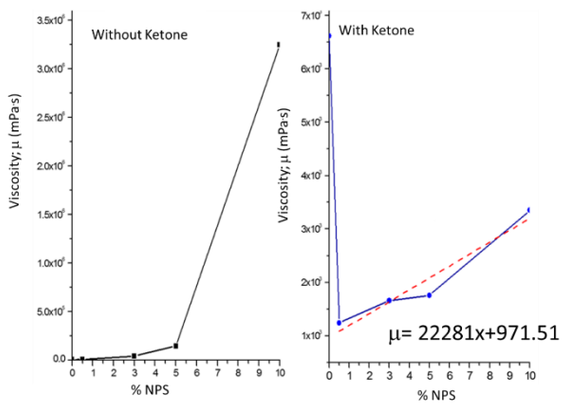

Figure 2 Effect of the NPS concentration on composite

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The addition of acetone to the formulations improves the dispersion of the particles in the polymeric matrix, so that the viscosity of the resin decreases and increases linearly with the silica content. Applying a linear regression, a linear determination coefficient of R2=0.9395 was obtained. Table 2 shows the percentages of viscosity decrease in the formulations studied, according to the linear behavior in the viscosity of these formulations, theoretically the viscosity of the resin (6614 mPa–s) is aligned with one loaded with 24% of nanoparticles adding acetone as solvent.

	Viscosity, μ (mPa–s)	% Diminish
Epoxy Polymer	6614	
0.5NPS/EP-A	1242	81.22
3NPS/EP-A	1658	74.93
5NPS/EP-A	1758	73.42
10NPS/EP-A	3350	49.34

Table 2 Viscosity decrease in NPS/EP with acetone addition

Figure 3 shows both low- and high-resolution scanning electron microscopy, comparing a coating formed only with epoxy resin, a commercial automotive anti-corrosion paint and the low silica content coatings of 0.5% (0.5NPS/EP-A) and the high silica content of 10% (10NPS/EP-A).

According to the image observed at low magnification (30X), the resin alone and with 0.5% silica form coatings with good covering capacity that preserves the initial roughness of the metal surface; however, the composite with high NPS content forms a structure with high roughness due to the formation of NPS agglomerates.

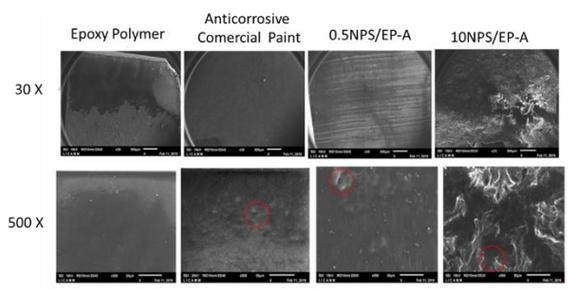

Figure 3 NPS dispersion into epoxy resin

ATR-IRFT NPS/EP Characterization

To determine the stability of the polymer resin with the silica nanoparticles, the spectra of the starting materials (aerosil or silica nanoparticles) and the epoxy resin after curing were obtained. The sum of these spectra results in the theoretical spectrum for NPS/EP (Figure 4). Where it shows that in the composites the signals corresponding to the polymer should be mostly retained and the band corresponding to the siloxane bonds of the silica is retained at 1100 cm^{-1}.

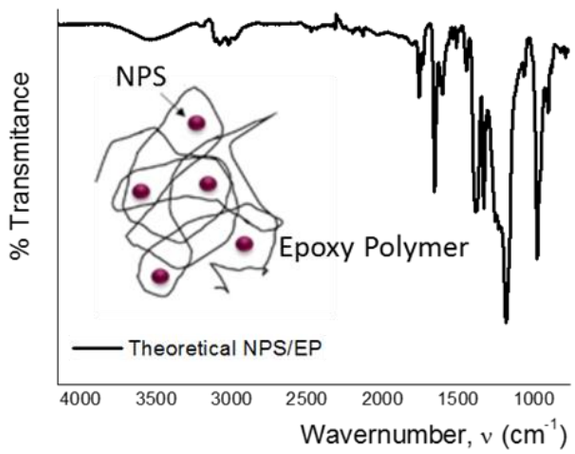

Figure 4 Theoretical ATR-FTIR for NPS/EP

Figure 5 shows the experimental plots obtained for the composites containing 0.3 to 10 % of nanoparticles with the addition of acetone as solvent. It can be observed that the silica nanoparticles are distributed in the polymeric matrix, this is determined according to the peaks of the spectra as they approach those of the aerosil (signal at 1000 cm–1) which indicates that the silica was perfectly integrated in the polymeric matrix. On the other hand, the experimental plots are very similar to the corresponding one for the theoretical composite reflecting that there is no interaction between the additive and the matrix that is causing the decomposition of the material.

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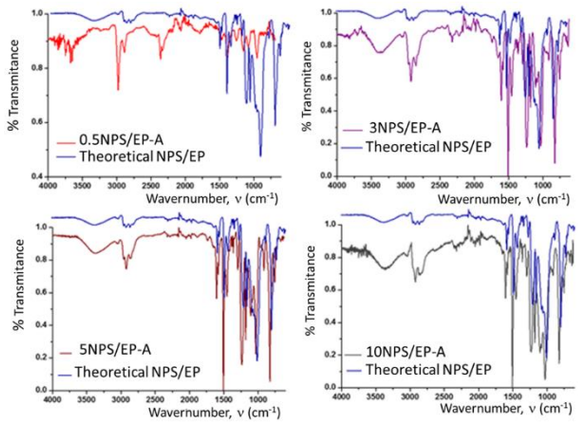

Figure 5 FT-IR for NPS/Epoxy Polymer

Adherence characterization

Among the most important physical properties to be evaluated in a coating is adhesion. This property is measured through the tensile stress required to achieve the detachment of the coatings. For these coatings, the required tensile stress reached 3 MPa for the nanoparticle-free epoxy resin coating. According to Figure 6, higher silica content increases the adhesion of the coatings, thus, the 0.5NPS/EP-A requires an average tensile stress to detach the coating of 3.62 MPa, while increasing the silica content to 10% (10NPS/EP-A) requires a tensile stress of 5.1 MPa to achieve the detachment of the deposited coating.

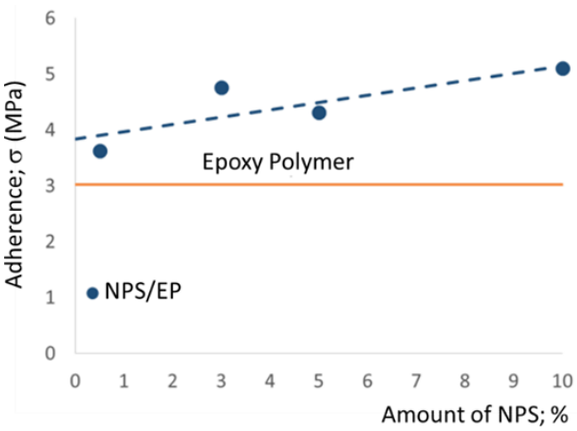

Figure 6 Adherence for NPS/EP

NPS/EP anticorrosion behavior

The anticorrosive performance of the coatings is determined from the corrosion rate values. These values are compared with the NACE (National Association of Corrosion Engineers) international criteria is specified in Table 3 (McCafferty E, 2010).

According to the results shown in Figure 6, the polymer resin has a poor corrosion resistance, since a corrosion rate of 107 MPY was obtained, while the A-36 steel presented a corrosion rate of 52.6 MPY having an acceptable corrosion resistance.

Corrosion Resistance	Corrosion Rate (MPY)
Extraordinary	<1
Excellent	1-5
Good	5-20
Admissible	20-50
Poor	50-200
Unacceptable	>200
*MPY= mils per year	

Table 3 Relative severity of corrosion rates

When silica nanoparticles were added, a significant improvement in the corrosion resistance of the polymer was observed, with corrosion resistance values ranging from good to outstanding. The composites with 0.5% silica and 5% silica showed good corrosion resistance with corrosion rates Vc of 7.08 and 13 MPY respectively. While the 10NPS/EP-A (10% silica) had excellent corrosion resistance with a corrosion rate Vc=1.42 MPY. Finally, the coating with 3% silica behaved as an outstanding corrosion protective barrier showing a corrosion rate of 0.472 MPY.

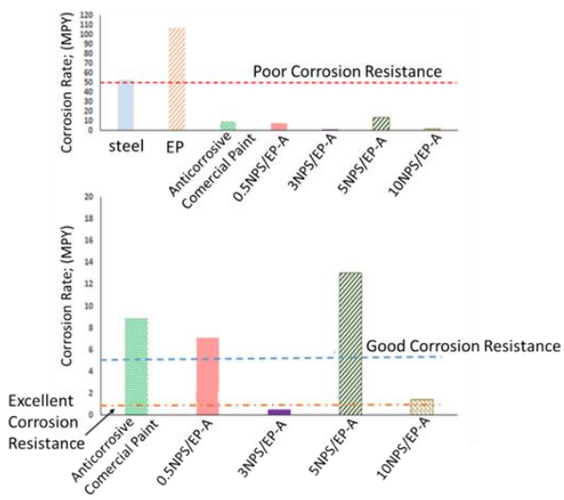

Figure 6 Corrosion rate for NPS/EP-A

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Conclusions

According to the results obtained in the tests carried out, it is concluded that silica is a good anticorrosive agent, in addition to the fact that it especially increased the properties and parameters that were measured in this project, such as adhesion (19 to 68%) and corrosion resistance (from poor to extraordinary).

The coating that showed the best results in the tests carried out was the coating with 3% silica using acetone as solvent.

References

Arcos D, Vallet-Regí M, Sol-gel silica-based biomaterials and bone tissue regeneration, Acta Biomaterialia (2010)6, 2874-2888. https://doi.org/10.1016/j.actbio.2010.02.012

Bierwagen G, Brown R, Battocchi D, Hayes S, Active metal-based corrosion protective coating systems for aircraft requiring no-chromate pretreatment, Progress in Organic Coatings (2010) 68, 48-61. https://doi.org/10.1016/j.porgcoat.2009.10.031

Danaee I, Darmian E, Rashed G.R, Zaarei D Self-healing and anticorrosive properties of Ce(III)/Ce(IV) in nanoclay–epoxy coatings, Iran Polym J (2014) 23, 891–898. https://doi.org/10.1007/s13726-014-0288-x

Dave P, Sirach R, Nanocomposites: Introduction, Synthesis and Applications. In Anticorrosive Nanomaterials. Verma CH, Mustansar H, ebenso E.E (Eds) (2022) pp. 15-43, The Royal Society Chemistry. ISBN: 978-1-83916-411-8

Grätzl T, Dijk Y. van, Schramm N, Kroll L. Influence of the automotive paint shop on mechanical properties of continuous fibre-reinforced thermoplastics, Composite Structures (2019) 208, 557-565. https://doi.org/10.1016/j.compstruct.2018.10.052

Groysman A, Capt. 2 Corrosion phenomena, Corrosion for Everybody, Springe (2010) New York, pag. 53-107. eBook ISBN: 978-90-481-3477-9.

Honarvar Nazari, M., Shi, X. (2016) Polymer-based nanocomposite coatings for anticorrosion applications. In M. Hosseini & A. S. H. Makhlouf (Eds.), Industrial Applications for Intelligent Polymers and Coatings. New York, Philadelphia: Springer Publishing, pp. 373-399. DOI:10.1007/978-3-319-26893-4_18.

Hung W.I, Chang K.Ch, Chang Y,H, Yeh J.M (2011). Advanced Anticorrosive Coatings Prepared from Polymer-Clay Nanocomposite Materials. In Advances in Nanocomposites Synthesis, Characterization and Industrial Applications. Edited by Dr. Boreddy Reddy (Ed.), ISBN: 978-953-307-165-7, InTech.

Kiliaris P, Pepaspyrides C.D, Polymer/layer silicate (clay) nanocomposites: An overview of flame retardancy, Progress in Polymer Science (2010) 35, 902-958. https://doi.org/10.1016/j.progpolymsci.2010.03.001

LeBaron P.C, Wang Z, Pinnavaia T.J, Polymer-layered silicate nanocomposites: an overview, Applied Clay Science (1999) 15, 11-29. https://doi.org/10.1016/S0169-1317(99)00017-4

Mahon J.R (2022) Experimental Characterization and Manufacture of Polymer Nanocomposite Dielectric Coatings for High-Temperature Superconductor Applications, Theses and Dissertations. Rowan University. https://rdw.rowan.edu/etd/3006.

McCafferty E, Introduction to corrosión science, Springer (2010) New York. eBook ISBN: 978-1-4419-0455-3

Percy M.J, Barthet C, Lobb J.C, Khan M.A, Lascelles S.F, Vamvakaki M, Armes S.P, Synthesis and characterization of vinyl polymer-silica colloidal nanocomposites, Langmuir (2000) 16, 6913-6920. https://doi.org/10.1021/la0004294

Salazar-Hernández C, Salazar-Hernández M, Juárez-Ríos H, Carrera-Cerritos R, Carrera-Rodríguez M, Elorza-Rodríguez E., Tratamientos empleados para evitar la corrosión. Ingeniería y Tecnología. Science Associated Editors (Diciembre 2015). ISBN 1-944162-05-4

ISSN 2523-6776

Salt Spray and Salt Fog Testing. ASTM B117

Wei T, Yan F, Tian J, Characterization and wear- and corrosion-resistance of microarcoxidation ceramic coatings on aluminum alloy, Journal of Alloys and Compounds 389 (2005) 169–176. https://doi.org/10.1016/j.jallcom.2004.05.084

Yang F, Nelson G.L, Polymer/silica nanocomposites prepared via extrusion, Polymer for advance technology (2006) 17, 320-326. https://doi.org/10.1002/pat.695

Yi-Chia H, Teng-Yuan L, Cheun-Guang C, Wha-Tzong, Anti-corrosion characteristics of polyimide/h-boron nitride composite films with different polymer configurations, Surface & Technology (2014) 260, 113-117. https://doi.org/10.1016/j.surfcoat.2014.09.043

Zhu Z, Tsai C.Y, Zhao M, Baker J, Sue H.J, PMMA Nanocomposites Based on PMMA-Grafted α-Zirconium Phosphate Nanoplatelets, Macromolecules (2022) 55(4) 1165-1177. https://doi.org/10.1021/acs.macromol.1c02337

Zou H, Wu S, Shen J, Polymer/silica nanocomposite: Preparation, characterization, properties and application, Chemical Review (2008) 108, 3893-3957. https://doi.org/10.1021/cr068035q..

ISSN 2523-6776