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Article

Anticorrosive SiO_2-PDMS ceramic coating: effect of viscosity and functional group on the siloxane chain

Recubrimiento cerámico anticorrosivo SiO_2/PDMS: efecto de la viscosidad y grupo funcional en la cadena siloxano

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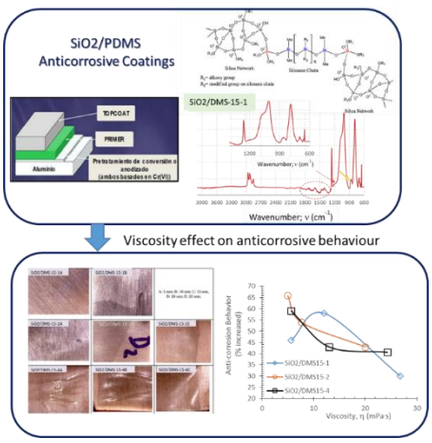
Abstract

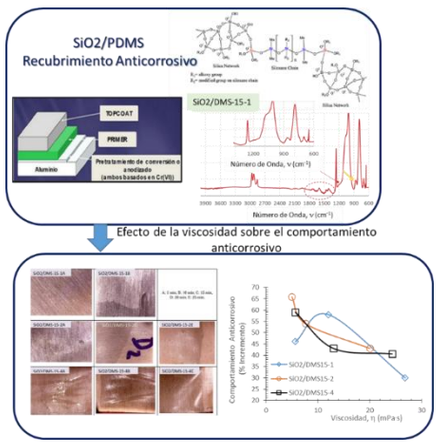
Nowadays, a variety of techniques exist for mitigating the effects of corrosion, including the use of anticorrosive coatings. In this study, we investigate the impact of viscosity on the final quality of a silica/PDMS-based ceramic coating, synthesized through sol-gel methodology. The polycondensation of tetraethylorthosilicate (TEOS) with polydimethylsiloxane (PDMS) was conducted at concentrations of 10, 20, and 40 wt.%, employing DBTL as a catalyst. The coatings were deposited on Al-6061 surfaces via immersion. Infrared spectroscopy indicates the integration of the inorganic phase (SiO_2; 1100 cm^{-1}, 720 cm^{-1}) with the siloxane chain (PDMS; 2900 cm^{-1}, 1250 cm^{-1}, 920 cm^{-1}, 785 cm^{-1}). As the siloxane chain length increased, modifications to the silica structure were observed, with the appearance of signals at 889 cm-1, 867 cm-1, and 835 cm-1. Conversely, the gelation times are reduced in proportion to the PDMS content in the sol solution. Therefore, to obtain smooth and homogeneous finishes, different gelation times are required when applying solutions with viscosities between 5 and 12 mPa·s. These coatings exhibited the most significant increase in corrosion resistance, reaching approximately 75%.



SiO_2/PDMS, viscosity, Corrosion mitigating, Infrared spectroscopy, Organic-inorganic coating

Resumen

Actualmente, existen diferentes métodos que mitigan los efectos de la corrosión, entre los cuales se encuentran los recubrimientos anticorrosivos. En este trabajo se reporta el efecto de la viscosidad sobre el acabado de un recubrimiento cerámico de base sílice/PDMS, que se obtiene mediante la metodología sol-gel, llevando a cabo la policondensación del tetraetilortosilicato (TEOS) con polidimetilsiloxano (PDMS) en concentraciones del 10, 20 y 40 % en peso, usando DBTL como catalizador. Los recubrimientos se depositaron sobre superficies de Al–6061 por inmersión. La espectroscopia de infrarrojo indica la integración de la fase inorgánica (SiO2; 1100 cm^{-1}, 720 cm^{-1}) con la cadena siloxánica (PDMS; 2900 cm^{-1}, 1250 cm^{-1}, 920 cm^{-1}, 785 cm^{-1}). Acorde con el incremento de la cadena siloxánica, se observó la modificación en la estructura de la sílice, apareciendo las señales a 889 cm^{-1}, 867 $^{-1}$ y 835 cm^{-1}. Por otra parte, los tiempos de gelificación se reducen en función del contenido de PDMS en la solución sol, por lo que, para obtener acabados libres de grumos y homogéneos, se requieren diferentes tiempos de gelificación al aplicar soluciones con viscosidades entre 5–12 mPa.s. Estos recubrimientos fueron los que mostraron un mayor incremento en la resistencia a la corrosión, de alrededor del 75%.



SiO_2/PDMS, Viscosidad, Reducción de corrosión, Orgánico-inorgánico cerámico, Espectroscopia de infrarrojo

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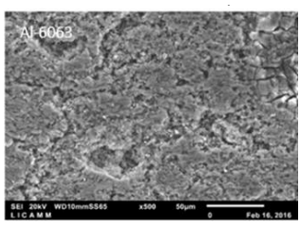
Introduction

Corrosion is a physicochemical phenomenon that causes the degradation of metals, resulting in the loss of physical properties, such as mechanical strength. In severe cases, corrosion can even lead to the complete degradation of the metal. The phenomenon of corrosion affects all metals and alloys utilized in industrial contexts. Figure 1a illustrates the impact of corrosion on an aircraft comprising an aluminum-silicon alloy (Al-6061) fuselage. In saline and humid conditions, these alloys are susceptible to intergranular corrosion (Figure 1b) (Benavides S, 2009; Zhang X, et. al, 2019). To mitigate the effects of corrosion on this metal, coatings are employed to protect the underlying material. These coatings are composed of an anodizing or anticorrosive layer (chromium and chromate base), a primer (organic phase with traces of chromates), and a topcoat (organic phase) or final finish (Cushman A.S, et. al, 1910; Swgelok 2024).

Box 1

(a)

(b)



(c)

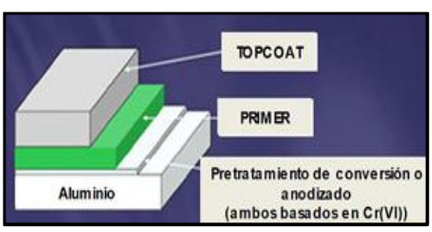


Figure 1

(a) Corrosion effects in an aircraft (take from https://aerocorner.com/blog/types-of-aircraft-corrosion/) (b) Intergranular corrosion in Al-6061 used in aircraft (take from Salazar-Hernández C, 2017) (c) Composition of a commercial anticorrosion coating (Take from Nace-International http://impact.nace.org/economic-impact.aspx).

At the industrial level, chromium anodizing is a common anti-corrosion agent. This involves the addition of a layer of chromium, which acts as a sacrificial anode. This means that the chromium is corroded by the metal being protected, thereby preventing corrosion. Despite the excellent anticorrosive properties of chromium, it is a toxic element that must be replaced by coatings that are more environmentally friendly (Olorunniwo P.P, 2014; Pellerin C, 2000) Recently, C. Salazar-Hernandez et al. (Salazar-Hernánde C, 2018; Salazar-Hernández C, 2019) have developed hybrid coatings based on silica and polydimethylsiloxane (PDMS). In these coatings, PDMS is cross-linked into the silica network (see Figure 2), which allows the synthesis of coatings with high mechanical stability, good adhesion, and good corrosion resistance on Al-6061. Others, anticorrosive coatings are compounds with organic and organic fragment, where the inorganic network increased the anticorrosive behavior or chemical stability (Ghogde N.R, 2024; Deng Y, 2024; Fu Y, 2022).

Box 2

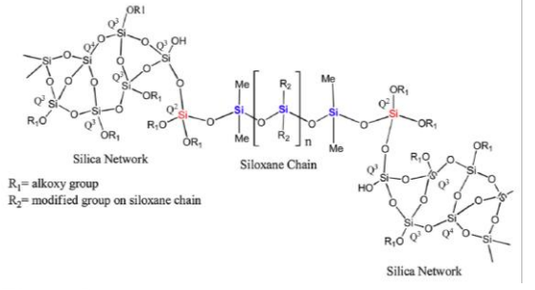


Figure 2.

Chemical structure of SiO_2/PDMS hybrid material
Source: (Salazar-Hernández C, 2019)

Experimental procedure

SiO_2/PDMS Ceramic Synthesis

The coatings were obtained via the sol-gel methodology, using tetraethylorthosilicate (TEOS; 99% purity; Fluka) as the starting reagent for silica formation and hydroxylated polydimethylsiloxane (DMS-15; GELEST; 99:12-32 cSt). To this purpose, a sol solution was prepared by mixing the quantities specified in Table 1 and adding 1 wt.% with respect to TEOS of dibutyldilaurate tin (DBTL; 95%, Aldrich), which served as a polycondensation catalyst, thereby facilitating the crosslinking of the silica functional group and the siloxane chains of PDMS.

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The sol solutions were heated to 50 °C and maintained at this temperature throughout the experiment. The change in viscosity over time was determined by measuring the viscosity with a Brookfield DV2RLV viscometer, using the UL adapter and controlling the temperature at 50 °C with a TC-650 recirculator.

Box 3

Table 1

Quantities used for the synthesis of the sol solution

	TEOS (g)	DMS-15 (g)
SiO_2/DMS-15-1	10	1
SiO_2/DMS-15-2	10	2
SiO_2/DMS-15-4	10	4

Application of SiO_2/PDMS to Al6061 samples

Thin sheets of Al-6061, measuring 3 mm in thickness and 2x3 cm in dimension, were cut. Prior to the application of the coating, the samples were subjected to abrasion with 600-grit sandpaper to remove any residual pollution. Subsequently, the samples were washed twice with distilled water and, finally, once with reagent-grade ethanol, with the objective of drying them in an oven at 50 °C for three hours. The coatings were deposited using the immersion technique, with an immersion speed of 1 mm/min, and were then left to dry at room temperature for 24 hours.

Coating Characterization

Infrared spectroscopy: Infrared spectra were obtained using a Thermo Scientific Nicolet iS10 ATR-FTIR instrument. The average of 32 scans was measured in a spectral window of 4000–600 cm^{-1}, with a resolution of 4 cm^{-1}.

Physical Characterization: Leeb hardness. Leeb hardness was measured using a UNI-T UT-347A instrument according to the recommendations of ASTM A956/A956M-17a.

Adhesion measurement: The force required to achieve peel of the coating was determined using the pull-off test method with a PosiTest AT-A instrument according to ASTM D4541.

Corrosion measurement

An evaluation of corrosion was conducted. Corrosion tests were conducted on a Peak Tech DIT-105 bench with a DCpower-2250 adapter.

In this configuration, the voltage and current generated in the galvanic pile formed by the Al/6061 plate with and without coatings as the anode, and graphite as the cathode, were measured. A 3.5% w/v NaCl solution with a pH of 3 was used, and to acidify, concentrated HCl was added dropwise. A constant current of 0.5 A was applied for 2 h, after which the weight loss generated was subsequently measured and the corrosion rate determined according to Equations 1 and 2 [6, 10, 11].

$$\boldsymbol{V_c = \frac{\Delta m}{A \cdot t} [=] \frac{kg}{m^2 \cdot s}} \quad (1)$$

$$\boldsymbol{V_{cp} = \frac{V_c}{\rho} = \left[\frac{mm}{a\tilde{n}o}\right]} \quad (2)$$

Results

Chemical characterization of SiO_2/PDMS ceramics

Figure 3 shows the spectrum corresponding to the SiO_2/DMS–15–1 modified ceramic, in which the formation of the silica network from TEOS is identified. The Si–O–Si bond is observed at 1010 cm^{-1} (signal A; intense and wide band) and at 720 cm^{-1} (signal A; low intense band). Furthermore, the integration of the DMS siloxane chain (–Si–O–Si–) is corroborated by the presence of the siloxane bond in the E signal at 920 cm^{-1} (small and broad) and at 785 cm^{-1} (intense and thin), as well as by the band at 1250 cm^{-1}, which identifies the Si-C bond (D signal). In the 2900–2700 cm^{-1} region, the $–CH_3$ groups of DMS–15 and the unreacted $–CH_2CH_3$ groups of the alkoxide were identified (signal B). Therefore, it can be concluded that the reaction conditions allow for the formation of crosslinks between the silica network formed by the silicon alkoxide and the siloxane chain fragments of PDMS (Launer P, 2013).

On the other hand; small board signals around the 1100 cm^{-1} was observed indicated the formation of different network silica size. These are remarked with circles and arrows; the different silica clusters are increased according to amount of siloxane chain that was added. Then, major modification in the size of silica network was obtained for ceramic with 40%p of DMS-15 (siloxane chain).

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According to infrared results a similarly structure to POSS/PDMS (polyhedral oligomeric silsesquioxane/polydimethylsiloxanr) was observed (Feng X, 2024).

Box 4

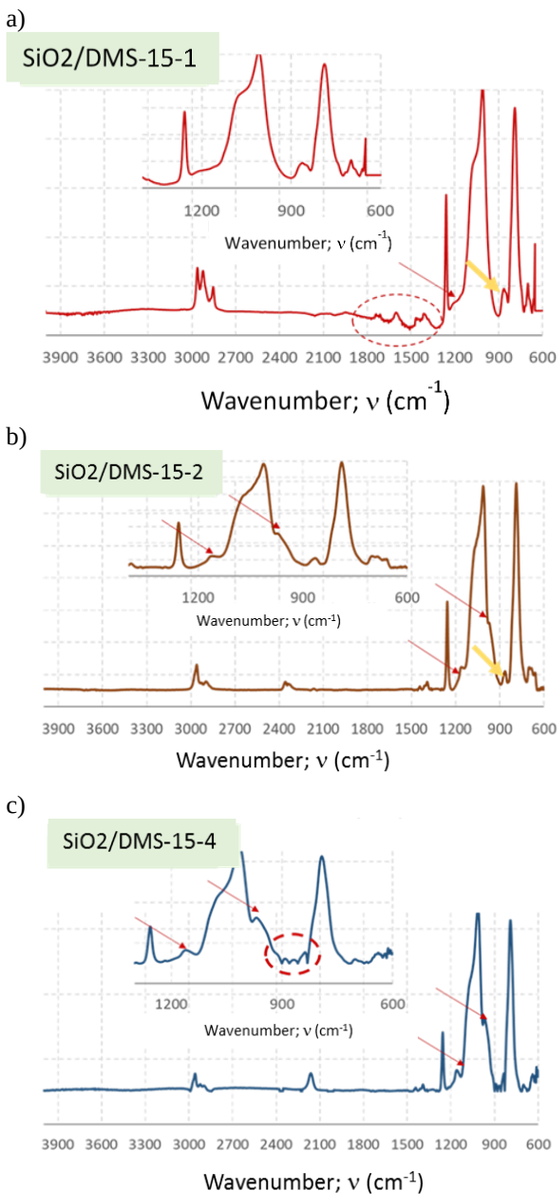

Figure 3
Effect of the siloxane chain in the hybrid ceramic structure (SiO2/DMS-15)

Effect of viscosity on the texture and physical properties of the coating

Figure 4a shows the effect of the siloxane chain on the gel point; where this was modified of 40 min (SiO2/DMS-15-1) to 20 min (SiO2/DMS-15-4) indicating an acceleration in the polycondentation between the silica fragments and the siloxane chain.

On the other hand, the Figure 4b shown the quality coating obtained for different viscosity; in the Figure 4c is indicated the impact of viscosity on the coating finish, as well as the siloxane chain content. At a mixing or gelling time of 10 minutes, the solutions behave as Newtonian fluids with a viscosity of approximately 5 mPa–s, forming thin coatings for concentrations of 10 and 20 wt.% PDMS. As the solid network forms, the viscosity increases, reaching a value of between 10 and 15 mPa–s. after 20 minutes. This results in the formation of thick coatings with clump formation at concentrations of 20 and 40 wt 7%, indicating an enhanced ability to coat the metal surface.

Box 5

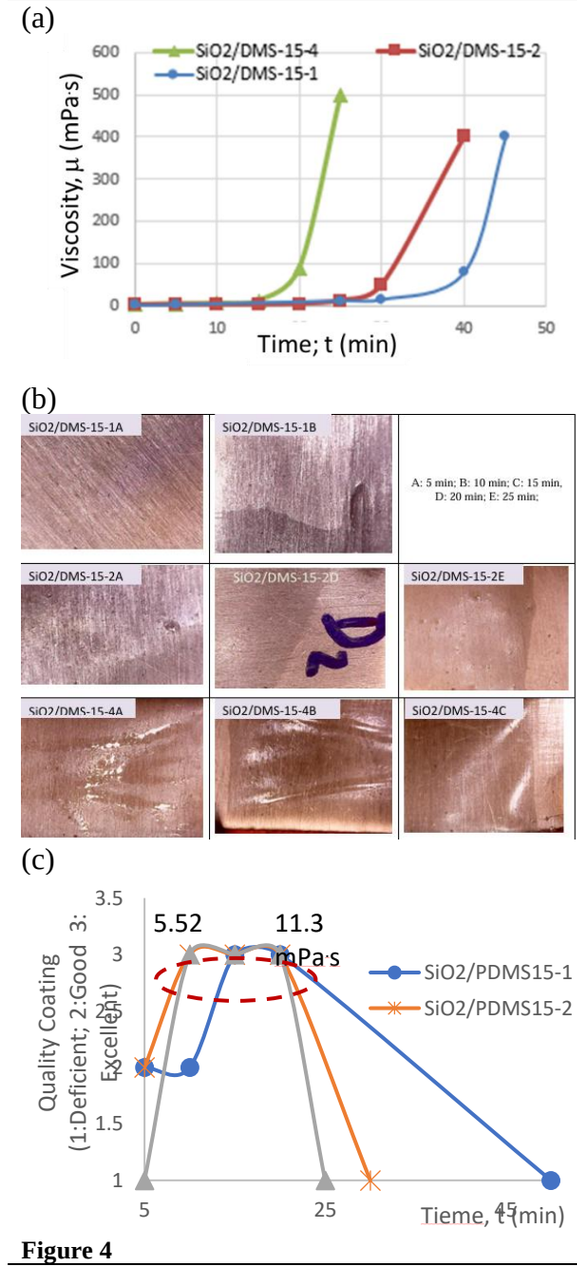

Figure 4
(a) Gelling curve for SiO2/DMS-15 ceramics (b) quality coatings obtained to different viscosity (c) effect of the viscosity on quality coatings

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Figure 5a shows the impact of PDMS content in the ceramic lattice on its adhesion. It was observed that as the amount of PDMS decreases the adhesion of the hybrid ceramic with the metal surface increases. In contrast, the hardness (Figure 4b) exhibited an inverse relationship, whereby an increase in hardness was associated with an increase in PDMS content in the ceramic structure. While both properties are crucial, adhesion should be a critical consideration in a coating, as a lack of strong interaction with the metal surface can result in removal and a diminished protective effect.

Box 6

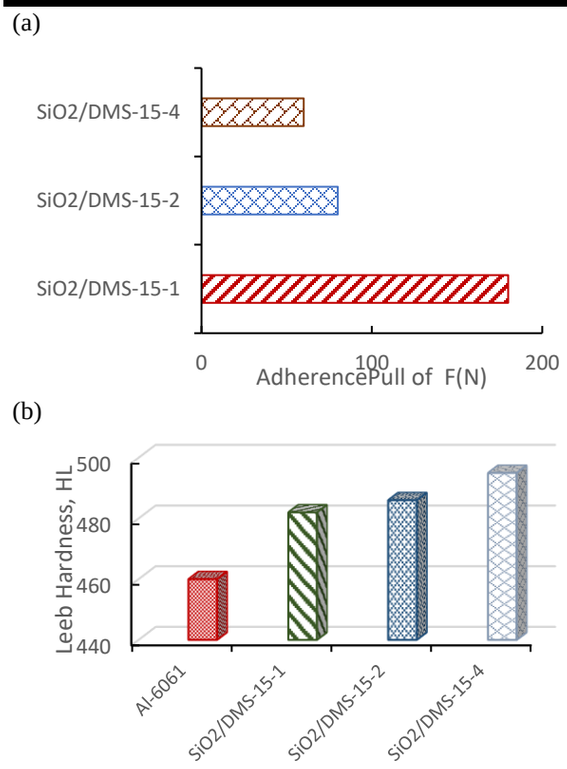

Figure 5
Physical properties of coatings with viscosities of 10–15 mPa–s (a) adhesion (b) Leeb hardness

Resistance to corrosion

Figure 6 shows the effect of viscosity on corrosion resistance. It can be observed that the highest corrosion resistance is obtained at a viscosity of approximately 10 mPa–s (10–15 min of gelation) for a PDMS concentration of 10 % in the siloxane chain, as this provides a surface finish that is superior to that of other concentrations.

For the 20 and 40 % concentrations of ceramics, the greatest enhancement in corrosion resistance was observed for a viscosity of approximately 5 mPa–s, which corresponds to a gelation time of between 5 and 10 minutes.

Box 7

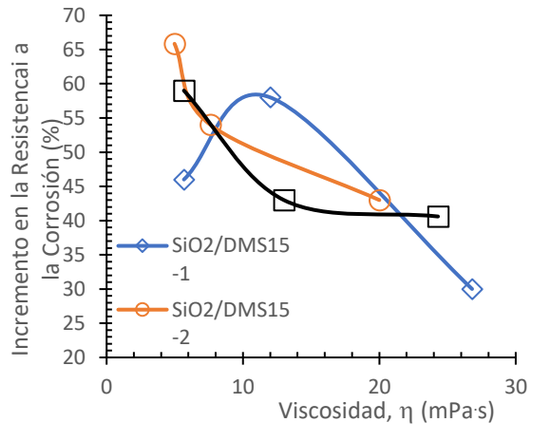

Figure 6
Effect of viscosity on corrosion resistance of Al-6061

Conclusions

The viscosity of the sol solution employed to obtain the coatings has an impact on the adherence and hardness of the ceramic deposited on the metal substrate. Deposits formed between 5 and 10 minutes of gelation (approximately 5–12 mPa–s) exhibit enhanced adherence and mechanical stability, as well as a greater degree of homogeneity. These coatings are free of clumps or very thin, and they do not completely cover the roughness of the metal.

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Statements & Declarations

Consent to participate and Consent for publication

The authors express their approval to participate and publish this work in ECORFAN Journal

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Conflict of interest

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

Author contribution

All authors contributed to the development and revision of the manuscript; CSH and MSH (conceptualization, interpretation and analysis date; writing and financial support); EER (interpretation and analysis date and methodology), JMMM (interpretation and acquisitions date). All authors read and approved the final manuscript.

Availability of data and materials

Indicate the availability of the data obtained in this research.

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Abbreviations

SiO_2	Silica ceramic
PDMS	Polydimethylsiloxane
SiO2/PDMS	Silica ceramic modified with polydimethylsiloxane
SiO2/DMS15-1	Silica ceramic modified with 10 % weight polydimethylsiloxane
SiO2/DMS15-2	Silica ceramic modified with 20 % weight polydimethylsiloxane
SiO2/DMS15-4	Silica ceramic modified with 40 % weight polydimethylsiloxane

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