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Sol-gel, one technology by produced nanohybrid with anticorrosive properties

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Abstract

The evolution of nanotechnology has been allowed modify the material properties since of chemical architecture. In this work, we development nanohybrids sol-gel process, silica particles are incorporated a functionalized polymer resin (type epoxy and/or phenolic) with carboxylic groups. When the metallic plate is coating formed film ceramic glass. The incorporation this particles into to polymeric matrix, allowed to obtain performance corrosive properties. The structural characteristics of the different materials prepared, phenolic resin (RF), the resin functionalized (RFF) and its corresponding hybrids (RF-SiO_2 and RFF- SiO_2), were studied by infrared spectroscopy and morphological changes were analyzed by scanning electron microscopy. Then cooper plates were coated with these materials to evaluate their corrosion performance. The corrosion performance evaluation for each of these coatings RF, RFF, RE-SiO_2 and RFF- SiO_2 were determined by the following tests: a misty saline chamber operated under accelerated corrosive conditions for corrosion advance measurement, abrasion and adhesion.

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Keywords: Functionalized phenolic resin; crystalline hybrid material; coating anticorrosive

1. Introduction

In this work, we report a novel approach for producing phenolic or epoxy functionalized resins substrates with Abietic Acid, and then reacted with silica particles, to yield a new hybrid (organic/inorganic) material [1,2].

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Inorganic-organic hybrid composites are rapidly emerging as alternatives to traditional anti-corrosion materials as they combine the chemical and mechanical properties of both inorganic and organic components [3]; because such coatings alone do not have sufficient corrosion protection properties for the density and thickness to provide protection to the metal surface[4,5].

The functionalized resins are still interesting from both technological and scientific points of view, as demonstrated by the inclusion of nanoparticles to improve properties of a Novolac-type or epoxy [6].

The idea to produce new materials is to predict the properties before producing the material, which leads to further expand knowledge in the area of hybrid materials [4.6]. In this paper we develop materials, by the sol-gel reaction to add silica particles functionalized with a polymer matrix, resulting hybrids of various functionalized polymeric resins, showing greater corrosion protection[7,8]. The functionalization is carried out in the presence of carboxyl groups, which allow a strong interaction between the polymer chains and the surface of the copper plate also allowing the formation of a coating film glass-ceramic. These properties were determined by different analytical techniques. Based on the results of their characterization, these materials may be of technological importance as a suitable control in the design of the experimental conditions, may develop a wide range of these new materials.

2. Experimental

2.1 Preparation of materials

The resin used in this study was synthesized by conventional route for the Novolac-type and was functionalized with carboxyl groups. The hybrid material composed of modified phenolic resin (FRR) and silica was prepared from ethanol solutions.

A large variety of hybrid materials were analyzed in this work. The following nomenclature is employed to facilitate identification of a given compound among the diversity of specimens: (i) RF(x)-SiO_2(y)/IC or (ii) RFF(x)-SiO_2(y)/IC, where x and y (x+y=100) represent the % weight of each phase in the corresponding hybrid product, and (ii) the addition of an inorganic acid or basic compound (IC) after the hybrid sol synthesis is denoted by HF, HCl, or NH_3, otherwise none of these latter symbols would appear. The synthetic method and preparation conditions for the modified resin (RFF)and hybrid materials has been described elsewhere[1].

2.2 Anticorrosive coating of Cu plates

Commercial copper plates (70x120x5 mm) were cleaned via ultrasound bath (Branson, model 3210). Polished Cu metal plates of 3” × 6” were coated with RF, RFF,RF-SiO_2 and RFF-SiO_2 films, respectively; RF and RFF coatings were applied from ethanol solutions while both RF-SiO_2 and RFF-SiO_2 hybrid substrates were applied as sols. The surface of each Cu plate was paint- brushed with the coating substance under study. Thermal treatment at 180°C of the above systems brought about both the curing of the resin as well as, in the case of hybrid systems.

2.3 Characterization techniques

The characterization of the resulting hybrid materials was carried by FTIR spectroscopy. Infrared analysis was done in a Bruker Vector 33 spectrometer. The morphology of hybrid materials was observed by Scanning Electron Microscopy (SEM) observations were carried in a Jeol JSM-5200 scanning microscope.

2.4 Corrosion tests inside a misty saline chamber

Corrosion tests developed on Cu plates covered with the PFR, FPFR, PFR-SiO_2, FPFR-SiO_2 films were run inside a Q-FOG Cyclic Corrosion Tester 1100 saline mist chamber, according to the ASTM

B117-07a standard. Each corrosion test proceeded continuously during 24h and 48h, the exposure time depending on the resultant intensity of the respective corrosion attack.

We assessed the time it took to appear at the first sign of corrosion on the plates, recording the number of hours for each applied coating. By ASTM D 1654-05, was evaluated peeling resistance of the coatings. Each of the coated copper plates were asked a scratch, from which detachment were measured maximum and minimum coating after 96 hours of the test.

2.5 Adherence and abrasion

The adhesion tests were performed on the coatings under the ASTM D 3359-02 Method B. The tests were conducted in triplicate on the dry coating. Cutting spaces were 2 mm and 6 cuts were made.

The abrasion tests were carried out under the ASTM D 4060-07, using a machine TABER Industries, Model 5050 abraser. The test conditions were of 57% relative humidity and temperature of 23°C, by triplicate on the coatings. The load applied by was 500 g, the number of cycles 100 and abrasive type CS-10.

3. Results and Discussion

3.1 FTIR spectral analysis

In this results the RFF, it is possible to observe the functionalization of the Novolac-type resin through of presence of the bands at 1737 cm^{-1} and 1610 cm^{-1} to belong to C=O asymmetric and symmetric vibrations of the carboxylic acid, respectively. The bands 1236 cm^{-1} and 1101 cm^{-1} are attributed to the vibration of the C-O-C bonds, whose identification with FT-IR spectroscopy has already been described[8,9]. For the silica pure, the bands for Si-O-Si symmetric and asymmetric vibrations are bands located at 794 cm^{-1} and 1112 cm^{-1}, respectively[9]. The band at 952 cm^{-1} corresponds to the Si-OH group[10,11] The band in the range from 3700-3000 cm^{-1} is attributed to the presence of hydroxyl groups in the samples. To the RFF(40)-SiO_2(60) hybrid, it is possible to observe a broad band region of 3600-3000 cm^{-1} is associated to OH groups of the ethanol, phenol and silanol groups[11]. The ester carbonyl groups observed at 1696 cm^{-1} are evidence of the reaction between the OH groups belonging to carboxyl groups of the RFF with the OH groups on the surface of the silanol groups[12], favored by the high electronegativity of oxygen and the readily available lone pair of electrons in the carbonyl group, and by the nature of the acidic feature of the SiOH group then polymer chains of RFF may be bonded by oxygen to silanol groups[7].

3.2 *Visual appearance of the hybrid and SEM*

A SEM photographic study of hybrid and non-hybrid materials was reported[1,8]. In this contribution provide a list of the materials characterized by SEM together with some important observations about the morphologies as well as with respect to some other optical or interesting properties of these solids.

In general, for these RF(x)-SiO_2(y) systems, we can observe that the molar RFF/SiO_2 ratio as well as the choice HF or HCL catalysts determine their optical (transparency or opacity) properties, who shows in the figure 2. At high SiO_2 contents, the resulting materials are mostly opaque especially if HF or NH_3 have been employed during the synthesis. In general, it seems that the lack of strong chemical interaction across the interface of silica particles and RF resin contributes in some way to the opacity displayed by many of these substrata (see figure 3 a-d).

The microstructure of RFF(x)-SiO2(y) hybrids exhibit special optical and morphological features (see Figure 4 a-d). Generally speaking, the aggregation extent of silica particles in the form of clusters that are distributed throughout the hybrid system; these SiO_2 cluster characteristics can induce phase separation thus influencing a great deal the optical properties of the system[1]. From the above we can say, both the

SiO_2 mean particle size and the interfacial properties between silica and RFF matrix allows obtaining either transparent or opaque materials depending on the preparation conditions. When the silica content is not too large, the hybrid materials are transparent-translucent specimens, independently of the catalyst used to promote gelation.

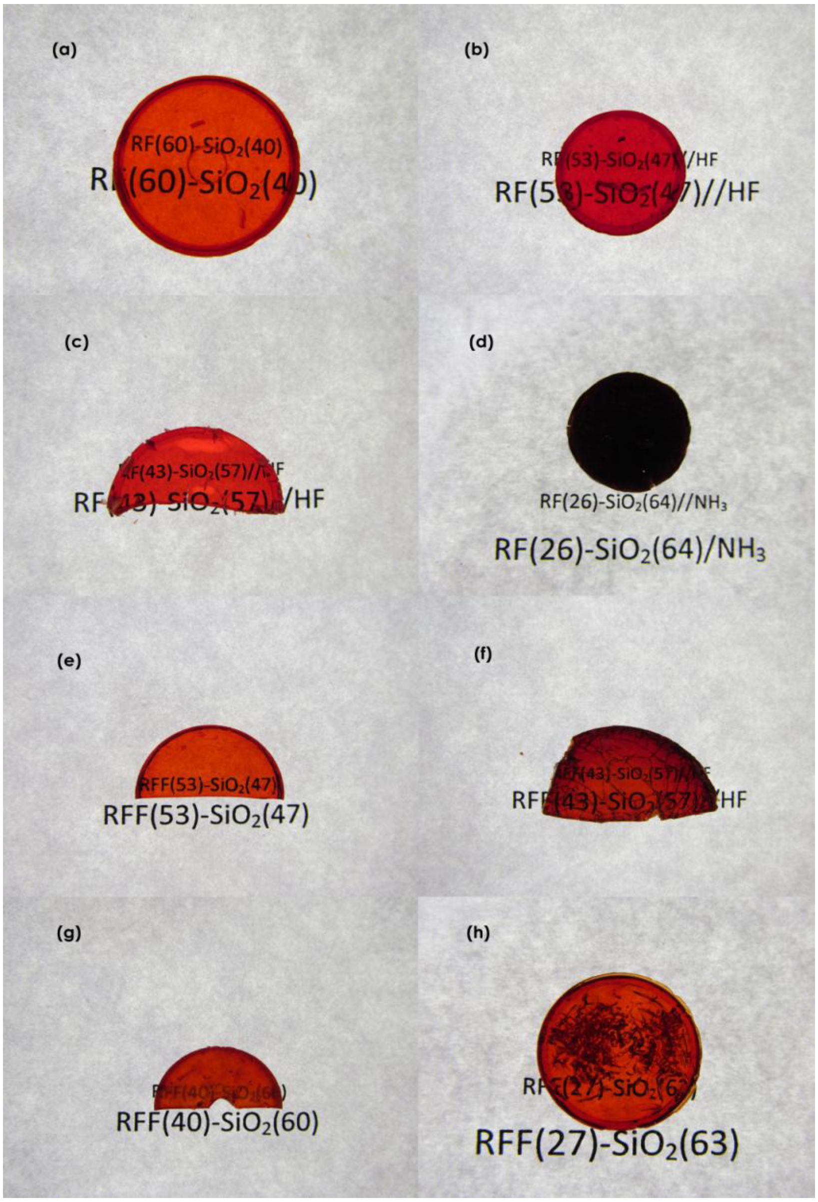

Figure 1. Photographs of (a) RF(60)-SiO_2(40), (b) RF(53)-SiO_2(47)//HF, (c) RF(43)-SiO_2(57)//HF, (d) RF(26)-SiO_2(64)/NH, (e) RFF(53)-SiO_2(47), (f) RFF(43)-SiO_2(57)//HF, (g) RFF(40)-SiO_2(60), and (h) RFF(27)-SiO_2(63) hybrid materials.

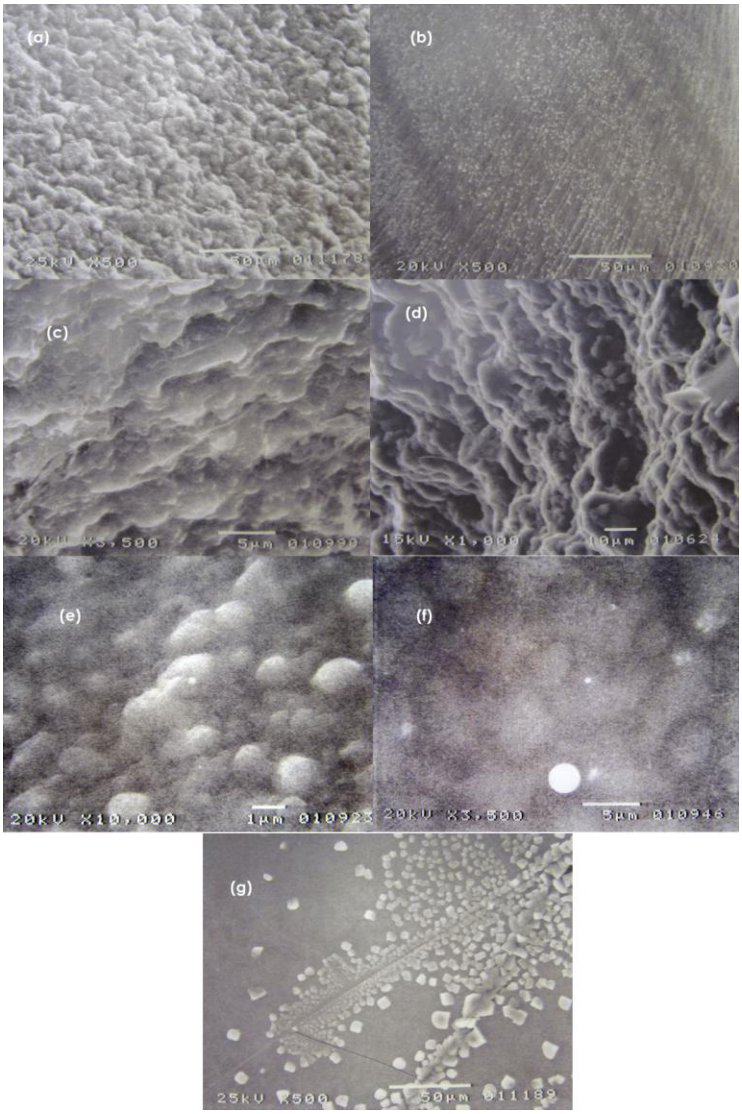

Figure 2. SEM micrographs of (a) RF(53)-SiO_2(47)//HF, (b) RF(43)-SiO_2(57)//HF and (c) RF(26)-SiO_2(64)/NH_3 hybrid materials (d) RFF(53)-SiO_2(47), (e) RFF(43)-SiO_2(57)//HF, (f) RFF(40)-SiO_2(60), and (g) RFF(27)-SiO_2(63) hybrid materials.

3.3 Visual aspects of resin-coated Cu plates after saline chamber corrosion tests

Figure 3 show a comparison of the macroscopic aspects of resin-coated Cu plates before the exposition of each of these substrates to the humid misty atmosphere of the saline chamber; these photographs were taken by means of a digital camera. From these photographs, it is clear that corrosion is much more intense in the plates coated with the RF-SiO_2 hybrid-covering (see Fig. 3b). On the other hand, the Cu plate coated with the RFF-SiO_2 covering (Fig. 3d) is the one that depicts the best corrosion endurance. The RF and RFF (Figs. 3a and 3c, respectively) correspond to intermediate corrosion-protection situations after the accelerated corrosion tests performed inside the misty saline atmosphere. Table 1 lists some important qualitative inferences concerning the saline chamber corrosion performance of the abovementioned coatings according to the visual evidence obtained from the surface aspects of Cu plates. The initial corrosion time is taken with reference to the apparition of corrosion centers of the Cu-plates surfaces, while the total corrosion time is the total time elapsed from the start to the end of corrosion tests performed on both resin-coated Cu plates.

The abrasion test results shows, that wear index (0.05 average) is minimum of the RF, FRR and RFF-SiO_2 materials, while that for hybrid RF-SiO_2 present 0.157 an increment due the coating does have adequate adhesion.

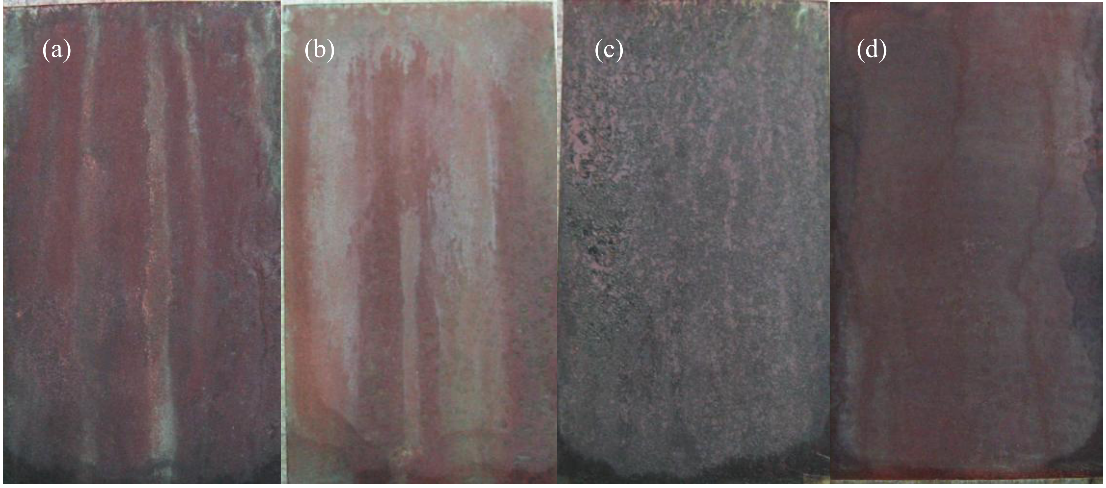

Figure 3. (a) Photographs of RF coated Cu surface after the saline chamber for accelerated corrosion testing. (b) Photographs of RF(43)-SiO_2(57)//HF coated Cu surface after the saline chamber for accelerated corrosion testing. (c) Photographs of RRF coated Cu surface after the saline chamber for accelerated corrosion testing. (d) Photographs of RFF(43)-SiO_2(57)//HF coated Cu surface after the saline chamber for accelerated corrosion testing.

Table 1. An example of a table Qualitative observations after the corrosion testing of coated Cu plates inside a misty saline chamber operating with a sprayed 5wt. % NaCl aqueous solution, relative humidity >95% and Temperature 35^0C.

Cu substrate coating	Initial Corrosion time/h	Total corrosion time/h	Observation
RF	48	96	Some slight surface corrosion is evident. The RF covering becomes somewhat greenish. The adherence is good after and before the tests. (Fig. 3a)
RF-SiO_2	24	96	No corrosion important. From initial scratch corrosion was not significant. Adherence was good despite there was partial removing of the coating film occur. (Fig.3b)
RFF	48	96	Slight corrosion together with some greenish coloring of the coating is observed. The adherence was better after test. (Fig.3c)
RFF-SiO_2	24	96	The coating film is homogenous, Practically no corrosion is developed The adherence is good after and before the tests. (Fig. 3d)

4. Conclusion

The above results demonstrate that organic-inorganic hybrid materials could be successfully synthesized from sol-gel processing of silica with the presence of modified phenolic hybrid. The characterization of the above substrates through various techniques, including corrosion tests, demonstrated the best performance of these innovative hybrid materials. The presence of the resin controls crystal growth influence the transparency and dispersion, thus reducing aggregation and agglomeration. Finally, we can say that the combination of silica and modified resins matrices by the method herein described, allows enhancing the stability of the material, resulting in a glassy hybrid ceramic-like material with unique properties.

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References

[1] Hernández-Padrón, G., Rojas, F., García-Garduño, M., Canseco, M.A. and Castaño, V.M. Development of hybrid materials consisting of SiO2 microparticles embedded in phenolic-formaldehydic resin polymer matrices. *Mater. Sci. Eng. A*2003;**355**:338-47.

[2] Sanchez C. Belleville P. Popall M. and Nicole L. Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to markets. *Chemical Society Review* 2011; **40**: 696-753.

[3] Mehdi A. Reye C. and Corriu R. From molecular chemistry to hybrid nanomaterials. Design and functionalization, *Chemical Society Review*2011; **40**:563-574.

[4] Hernández-Padrón, G., García-Garduño, M., Canseco, M.A. and Castaño, V. M. Nanoparticles-Based phenol-formaldehyde hybrid resins. *Journal Nanoscience Nanotechnology*2008;**8:**3142-5.

[5] Zou H., Shishan W. and Jian S. Polymer/silica nanocomposites: preparation, characterization, properties and applications. *Chemical Reviews* 2008;**108**:3893-3957.

[6] Hernández-Padrón G. García-Garduño M. and Rojas-González F. Hybrid materials based on functionalized epoxy resin netwoks. *Pigment and Resin Technology*2010; **39**: 195-202.

[7] Zheludkevich, M. Sol-gel coatings for corrosion protection of metals. *Journal of Materials Chemistry*2005;**15**:5099-6011.

[8] Hernández-Padrón G. Rojas F. Castaño V. Development and testing of anticorrosive SiO2/phenolic–formaldehydic resin coatings. *Surface & Coatings Technology*2006; **201**:1207–14.

[9] Colthup B., Daly H., Wiberley E. Introduction to Infrared and Raman Spectroscopy. 3rd.ed., Sn. Diego Cal:Academic Press; 1990.

[10] K. Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Jhon Wiley & Sons; 1962.

[11] Schrader Bernhard. Infrared and Raman Spectroscopy Methods and Applications. Germany:VCH; 1995.

[12] R. A. Niquist. Intepreting Infrared, Raman and Nuclear Magnetic Spectra. London: Academic Press; 2001.