

## Anticorrosive hybrid materials prepared by Sol-Gel Process

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### ABSTRACT

In this work, polymeric epoxy (ER) or phenolic-formaldehydic (PFR) matrix hybrid materials of silica particles were researched and characterized. These hybrid materials were prepared by means of the sol-gel process, where the polymeric matrix has been functionalized with carboxylic groups. The presence of this functional group allows the chemical union between the organic matrix and the inorganic modifier, which provides better properties to the new hybrid material. These resins are of low cost and improve elongation resistance and dimensional stability to metals. Functionalization provides major hardness and adhesiveness to resins. On the other hand the silica particles provide major thermal stability to the polymeric matrix. Due to these new properties these hybrid materials might be used as anticorrosive metal binders. These anticorrosive hybrid materials were evaluated by means of accelerated weathering by means of a saline cloud chamber. The morphology and changes in the structure were studied by means of electronic microscopy of sweeping and spectroscopic techniques.

**Keywords:** Phenolic-formaldehydic resin, epoxy resin; functionalized epoxy resin; hybrid SiO<sub>2</sub>-epoxy resin materials, SiO<sub>2</sub>/phenolic-formaldehydic hybrid systems, anticorrosive coatings, Misty saline chamber corrosion tests, abietic acid.

### Introduction

In this work, PFR-SiO<sub>2</sub>, FPFR-SiO<sub>2</sub>, ER-SiO<sub>2</sub> and FER-SiO<sub>2</sub> hybrid coatings are prepared by the sol-gel technique [1] employing, jointly with the TEOS reagent, either a precursor resin (PFR, FPFR, ER or FER) dissolved in ethanol. The presence of finely divided inorganic particles, e.g. silica, chemically attached to organic chains of a functionalized resins, offers the possibility of creating coatings of enhanced thermal and mechanical properties. This can be due to the chemical bounding of the FPFR or FER molecules on the SiO<sub>2</sub> surface by reaction with the silanol groups existing on the silica particles. These characteristics, together with the adherent properties of PFR and FPFR

how the same fore ER and FER resins, redound in the creation of effective barriers against corrosion of metallic substrates.

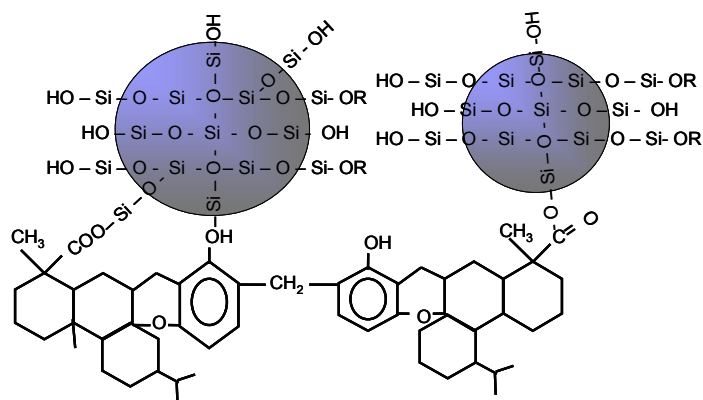
The objectives of this work are: (i) to describe the preparation of anticorrosive coatings made of non-hybrid PFR, FPFR, ER and FER and their corresponding hybrid materials; and (ii) to expose a series of similar Cu plates, coated with each one of these coatings, to the corrosive atmosphere of a misty saline chamber; (iii) to optically realize the anticorrosive properties of each system by SEM microscopy; and (iv) to realize the existence of chemical groups or bonds by FTIR spectroscopy.

## Experimental

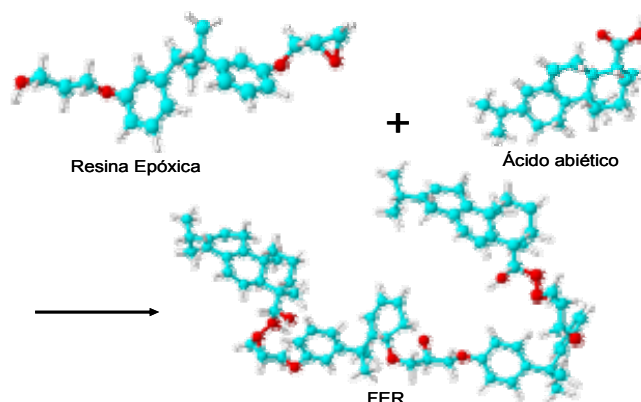
### *Phenolic-formaldehydic resin. Synthesis and -COOH functionalization [2]*

The resin used in this study was synthesized through the conventional route employed for a Novolac-type material. The FPR resin was prepared from a mixture of formaldehyde (F) and phenol (P) under an F/P molar ratio of 0.7. The catalyst (C) employed for the polymerization reaction between F and P was oxalic acid supplied according to a C/P molar ratio of 0.014. The F+P+C reacting mixture was mechanically stirred and refluxed during 5 h, to eventually obtaining the PFR compound. In order to prepare the FPFR material, abietic acid (AA) was incorporated into the F+P+C reaction vessel after 2 h of refluxing time, by employing a P/AA molar ratio of  $3 \times 10^{-3}$ ; the refluxing was then continued for further 3 h. The functionalized FPFR material acquired a distinctive coloration in-between the yellowish color of abietic acid and the reddish color of the PFR resin.

### *Preparation of PFR-SiO<sub>2</sub> and FPFR-SiO<sub>2</sub> Hybrid materials [3].*



### *Synthesis of unfunctionalized and functionalized epoxy resins*



### *Preparation of epoxy resin-SiO<sub>2</sub> hybrid materials*

The SiO<sub>2</sub>-ER and SiO<sub>2</sub>-FER hybrid materials, constituted by silica spheres distributed inside an ER or FER thermosetting network, were synthesized as follows. Initially, a mass of 5 g of ER or FER resin was dissolved in 20 cm<sup>3</sup> of ethanol; a second mixture involving TEOS (1.15 – 5.0 cm<sup>3</sup>, the exact quantity depending on the desired final molar composition) and water (2 cm<sup>3</sup>) together with ethanol (10 cm<sup>3</sup>) was prepared separately. The two solutions were then poured together into a glass flask and the resulting mixture was subjected to vigorous stirring and kept under reflux for one hour. The molar amount of TEOS was varied from 0.5 to 2.5 in order to obtain an assortment of SiO<sub>2</sub>-ER and SiO<sub>2</sub>-FER hybrid materials. The hybrid compound obtained this way can gellify if allowed to rest for several days. The SiO<sub>2</sub>-ER hybrids prepared from 0.5-2.5 moles of TEOS become transparent gels while the FER-SiO<sub>2</sub> materials evolve to yellow-translucent gels if 0.5-2.2 moles of TEOS are employed. When the amount of TEOS involved in the preparation of SiO<sub>2</sub>-FER is larger than 2.5 moles, an opaque-white precipitate is obtained.

### *Anticorrosive coating of Cu plates*

Polished Cu metal plates of 3" × 6" and  $4.895 \times 10^{-2} \pm 0.00005$ " thick, were coated with PFR, FPFR, PFR-SiO<sub>2</sub>, FPFR-SiO<sub>2</sub>, ER, FER, ER-SiO<sub>2</sub> and FER-SiO<sub>2</sub> films, respectively; PFR, FPFR, ER and FER coatings were applied from ethanol solutions while both PFR-SiO<sub>2</sub>, FPFR-SiO<sub>2</sub> and ER-SiO<sub>2</sub> and FER-SiO<sub>2</sub> hybrid substrates were applied as sols. The surface of each Cu plate was paint-brushed with the coating substance under study. The thickness of the film is  $7.5 \times 10^{-3} \pm 0.00005$ ". Thermal treatment at 180°C of the above systems brought about both the curing (polymerization) of the resin as well as, in the case of hybrid systems, the reaction between the -COOH groups (existing in the functionalized

FPFR and FER resin) and the silanol (Si-OH) species anchored on the surface of the SiO<sub>2</sub> globules.

#### *Corrosion tests in a misty saline chamber*

Corrosion tests developed on Cu plates covered with the PFR, FPFR, PFR-SiO<sub>2</sub>, FPFR-SiO<sub>2</sub> films were run inside a Singleton PSS-22 saline mist chamber, according to the ASTM B117 standard. Each corrosion test proceeded continuously during 24h, 48h or 72h, the exposure time depending on the resultant intensity of the respective corrosion attack.

### **Conclusions**

The SiO<sub>2</sub> particles are produced "in situ" by the sol-gel process and dispersed in the gel mass before the resin is eventually cured. It appears to exist an optimal amount of SiO<sub>2</sub> particles that favors an efficient covalent bonding between SiO<sub>2</sub> particles and epoxy or phenolic-formaldehydic resin as well as the original gelling of the hybrid materials. FER and FPFR coatings offer a reliable option against corrosion of metallic bodies. It appears that the adherence of a PFR or FER resin is significantly improved when this material is functionalized with carboxylic groups to render functionalized resins. The hybrid systems are the one showing the best corrosion endurance[4], this is likely due to the strong interaction existing between the COOH functionalized phenolic-formaldehydic or epoxy chains and the Cu surface then resulting in a kind of glassy ceramic-like impervious coating film. These coatings possess also a remarkable transparency, something that is not easily attainable with conventional coating substances.

### **Acknowledgements**

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### **References**

- [1] G. Hernández-Padrón, F. Rojas, R. Nava, R. Lima, V. Castaño, *Advances in Polymer Technology*, 21,(2002), 116.
- [2] G. Hernández-Padrón, F. Rojas, M. García-Garduño, M. A. Canseco and V. Castaño, *Materials Science & Engineering: A*, 355, (2003), 338.
- [3] G. Hernández-Padrón, F. Rojas, and V. Castaño, *Nanocomposites*, 15, (2004), 98.
- [4] G. Hernández-Padrón, M. García-Garduño, M. A. Canseco and V. Castaño, (2008) *Journal Nanoscience Nanotechnology*, 8 (6), 3142-3145.