

Anticorrosives, encapsulates, catalytic supports and other novel nanostructured materials

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Abstract. A phenolic-formaldehydic resin (PFR) of the Novolac-type and modified through the attachment of carboxylic end groups (MPR), is used to tailor the morphological and optical properties of sol–gel synthesized silica materials. Silica microparticles are produced from alkoxide precursors in the presence of PFR or MPR resins, leading to a final material consisting of SiO₂ globules entangled inside a polymerized resin matrix. Under appropriate experimental conditions, chemical bonds can be established between the SiO₂ silanol surface groups and the MPR carboxylic chains, to render SiO₂/MPR core-shell-type compounds. The presence of PFR or MPR resins during the sol–gel production of silica microspheres allows to control: (i) the sizes of final SiO₂ particles and (ii) the transparency or opacity properties of the final hybrid products. In this way, either opaque or transparent solid substrates can be obtained, depending on the amounts of reactants used to prepare the hybrid specimens. Solid MPR and SiO₂/MPR samples were characterized by infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy to determine chemical and textural properties of the hybrid substrates. Under appropriate experimental conditions, chemical bonds could be established between the SiO₂ silanol surface groups and the MPR carboxylic chains, to render SiO₂/MPR core-shell-type compounds.

Keywords. Sol–gel process; modified Novolac resin; stearic acid; abietic acid; corrosion; clear/translucent hybrid materials.

1. Introduction

The demanding applications of today's technology require proper scientific criteria for selecting an adequate resin for specific applications (Novak 1993; Hillmyer 2005). Of particular relevance are the tribological properties of polymers, which have become important for the synthesis and/or characterization of resin-based composites (Wilkes *et al* 1990). This key surface property is crucial for the performance of materials in many practical applications. In this work, we report a novel approach for producing PFR functionalized substrates with stearic acid (SA) or abietic acid (AA) and then reacted with silica nanoparticles (nanoSiO₂), to yield a new hybrid (organic/inorganic) material.

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 (Wang *et al* 2011); because such coatings alone do not have sufficient corrosion

protection properties for the density and thickness to provide protection to the metal surface. Thus, performance of corrosion resistance and stress resistance of lining materials can be improved by the incorporation of new hybrid composite.

Phenol–formaldehyde resin (PFR) was the first commercial synthetic resin and it is still one of the most common engineering materials nowadays, due to its attractive cost-performance relationship for applications ranging from laminates to coatings. PFRs 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 PFR (Dimitriev *et al* 2008). In the latter, the phenol–formaldehyde Novolac resin was modified with carboxylic groups to form a hybrid material *in situ*, using the sol–gel technique (Li and King 1994). This di-functionalized hybrid material was employed as a corrosion-resistant coating for copper plates (Hench and West 1990; Haraguchi *et al* 1998a).

In the present article the aim was to produce novel hybrid organic–inorganic materials; the classical sol–gel reaction has been modified to prepare hybrid materials incorporating either functionalized monomers or polymers

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(Sanchez and Livage 1990). The functional groups can fully or partially react with the hydrolysis products of the metal alkoxides in order to incorporate the polymer or monomer of interest. By this technique, a new family of materials can be synthesized by combining features of the inorganic sol-gel alkoxide moieties with those of a variety of organic or inorganic species (McCormick 1994).

Sol-gel chemistry, which is mainly based on inorganic polymerization reactions leading to a macromolecular oxide network, has provided a route to produce organic-inorganic hybrid materials at low processing temperatures (Ahmad *et al* 1994). By using organic materials such as alkoxides as starting components, incorporation of inorganic metal oxides such as silica, titania and zirconia into a variety of polymers, has been achieved (Kaserman *et al* 1994; Schubert *et al* 1994). The result is a reinforced inorganic-polymer hybrid having much improved thermal and dimensional stabilities (Hultsch 1948). Organically-substituted silicate materials are prepared by sol-gel processing of alkoxy-silanes in which the (functional) organic group is directly bonded to silica (Whang *et al* 1997). The organic moieties retained in the final material can modify or functionalize the oxide base material (Zou *et al* 2008). Although high potential of such hybrid materials is becoming more and more obvious, there have been only very few efforts for preparing inorganic-organic hybrids.

One of the great advantages of the sol-gel process is the preparation of thin films which have been widely used as coatings to increase wear and abrasion resistance (McCormick 1994).

Hybrid coatings have been proposed within the development of new nanomaterials with a discrete phase of nanoparticles and organic matrix of phenolic resin, which must be chemically modified to create similar sites that can bind to the hydroxyls of the silica particles, so that, in the present work, abietic acid and stearic acid were used to modify the surface attachment of the phenol-formaldehyde resin into silica sols resulting indeed in interesting new properties, as it will be shown below.

2. Experimental

2.1 Materials

All samples were prepared by using tetraethylorthosilicate (TEOS) (Aldrich Chem., 97 %), CO₂-free triple distilled water, ethanol (reactive grade) (J.T.Baker), the Novolac-type resin with phenol (Aldrich Chem.) (>99 %), formaldehyde (37 % aqueous solution, Aldrich Chem.) and oxalic acid (Aldrich Chem.).

2.2 Preparation of PFR functionalized with abietic acid

The resin used in this study was synthesized by the conventional route followed for attaining the Novolac-type and was functionalized with carboxyl groups. The Novolac-type

phenol resin was mixed with formaldehyde (F) and phenol (P) at an F/P molar ratio of 0.7 and catalyzed (C) by oxalic acid under a molar ratio C/P of 0.014. The mixture was mechanically stirred and refluxed for 5 h. After 2 h, abietic acid (AA) was added at a molar ratio of P/AA of 3×10^{-3} . The synthesis method and preparation conditions for the modified resin (MPR) have been previously described (Hernandez-Padron *et al* 2000).

2.3 Preparation of PFR functionalized with stearic acid

A phenolic-formaldehyde resin (PFR), of the Novolac family, was synthesized through the conventional route for these resins and then functionalized with carboxylic end groups to produce stearic acid-functionalized resins (MPR-SA). The detailed methods for the synthesis of conventional (PFR) and modified resins (PFR-SA) have been described elsewhere (Hernandez-Padron *et al* 2003, 2004, 2006, 2010). These procedures basically consist of the following steps: first, the unmodified Novolac resin was prepared through careful mixing of formaldehyde (F) and phenol (P) at an F/P molar ratio of 0.79, followed by dropwise addition of a solution containing 1.5 g of oxalic acid, dissolved in 50 cm³ of water. This initial mixture was refluxed for 30 min and then a solution, containing 1.0 g of stearic acid (SA) in 50 cm³ of water, was poured into the reaction flask and the resulting mixture was kept under reflux for 24 h.

The modified PFR (MPR)/nanoSiO₂ hybrid material was obtained from solutions of MPR in a mixture of ethanol and H₂O, respectively; afterward, the hybrid specimen was allowed to react with the silica nanoparticles. The amount of alcohol in the latter mixtures corresponds to half of the total volume employed in the overall synthesis, whereas the moles of water were equivalent to two thirds of the moles of ethanol. TEOS was dissolved in a separate glass beaker containing a volume of ethanol equal to the amount chosen to prepare the above MPR solutions. Then, the MPR water-ethanol solution was added to the beaker containing TEOS + ethanol mixture. The reactant mixture was kept under stirring and refluxing conditions for 5 h, to finally obtain the MPR/nanoSiO₂ hybrid systems. TEOS:MPR weight ratio employed in the above preparations was 1.5.

The above samples were dried at room temperature at 100 °C for 30 min at a heating rate of 0.5 °C/min and 200 °C for 2 h at a heating rate of 2 °C/min.

2.4 Characterization techniques

The characterization of the resulting hybrid materials was carried out by FT-IR technique. Infrared analysis (FT-IR) was done in a Nicolet 510 spectrometer, with an Ar laser by using the diffuse reflectance technique with pellets mixed with KBr (1:2 wt, hybrid material : KBr).

Scanning electron microscopy (SEM) observations were carried out in a Jeol JSM-5200 scanning microscope. The samples were coated with carbon by vacuum evaporation.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses were carried out in a DuPont 951 instrument operated in an air atmosphere at a rate of 10 K min^{-1} .

2.5 Anticorrosion coating of Cu plates

Polished Cu metal plates, of $364.89510^{-2} \pm 0.00005$ in, were coated with MPR (AA or SA), and nanoSiO₂/MPR films, respectively. MPR and hybrids coatings were applied from ethanol solutions whereas the nanoSiO₂/MPR hybrid solution was applied as a sol. The surface of each Cu plate was brush-painted with the corresponding coating. The thickness of the resulting film was $7.5 \times 10^{-3} \pm 0.00005$ in.

3. Results and discussion

FT-IR spectroscopy results are shown in figure 1, where figure 1(a) corresponds to the MPR-AA resin, figure 1(b) to pure silica and figure 1(c) to SiO₂/MPR-AA hybrid. In

the spectrum of MPR-AA, it is possible to see functionalization of the Novolac-type resin which is revealed through presence of bands at 1710 cm^{-1} and 1680 cm^{-1} that belong to C=O asymmetric and symmetric vibrations of the carboxylic acid groups, respectively. The bands at 1236 cm^{-1} and 1110 cm^{-1} are attributed to the vibration of the C–O–C bonds, whose identification with FT-IR spectroscopy has already been described (Orcel *et al* 1986; Colthup *et al* 1990).

The spectrum of pure silica is observed in figure 1(b). The band at 1633 cm^{-1} is associated with the deformation of molecular water. The bands for Si–O–Si symmetric and asymmetric vibrations are located at 794 cm^{-1} and 1104 cm^{-1} , respectively (Colthup *et al* 1990). The band at 963 cm^{-1} corresponds to the Si–OH group (Martinez *et al* 1998). The band in the range from $3800\text{--}3000\text{ cm}^{-1}$ is attributed to the presence of hydroxyl groups in the samples (Schrader 1995). The bands at 2929 and 2900 cm^{-1} are assigned to the organic groups of ethanol (Colthup *et al* 1990).

Figure 1(c) corresponds to the SiO₂/MPR-AA hybrid, where it is possible to observe a broad band region at

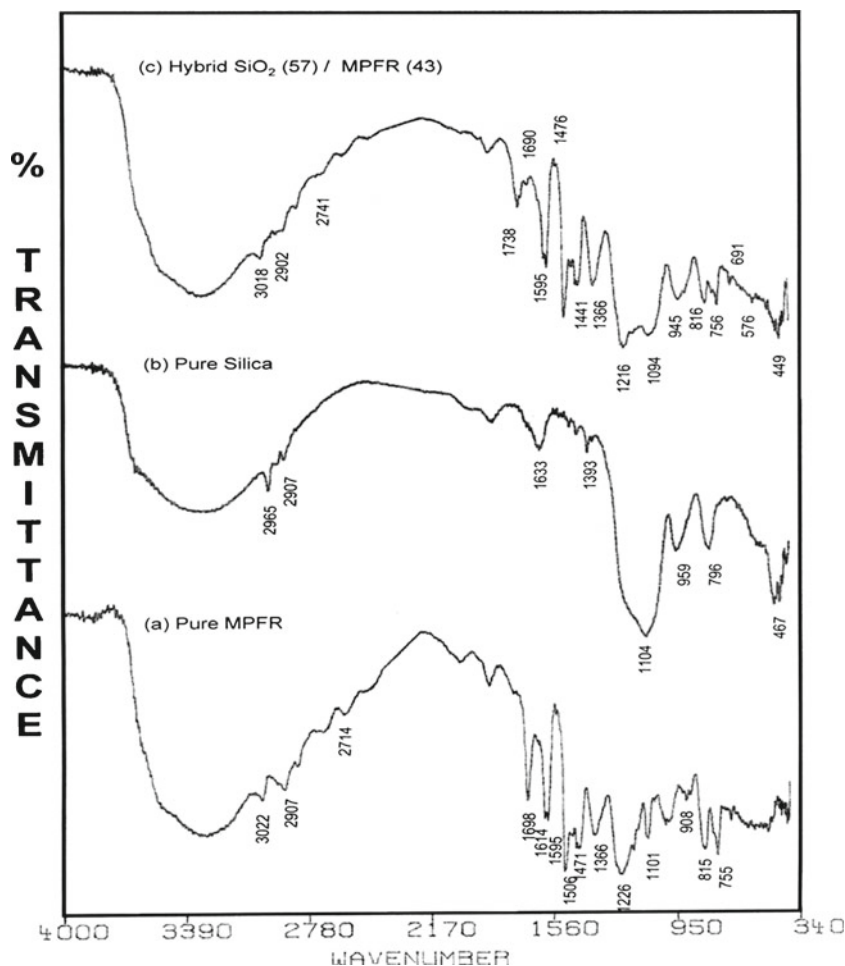


Figure 1. FT-IR spectra of (a) MPR-AA, (b) pure silica and (c) SiO₂/MPR-AA hybrid material.

3600–3000 cm^{-1} associated with the OH groups of ethanol, phenol and silanol groups (Smith 1998). The CH stretching of the phenyl rings is usually observed in the 3100–3000 cm^{-1} region (Pecksok and Shelds 1990). The ester carbonyl groups observed at 1696 cm^{-1} are evidence of the reaction between the OH groups belonging to the carboxyl groups of the MPR with the surface OH of the silanol groups (Dimitriev *et al* 2008); this reaction is favoured by the high electronegativity of the oxygen atoms and the readily available lone pair of electrons in the carbonyl group, and by the acidic nature of the SiOH group therefore, polymer chains of MPR–AA can be bonded by oxygen to silanol groups.

This novel material exhibits very different features in terms of microstructure, related to the transparency of these hybrids. Generally speaking, the aggregation of silica in the hybrid system changes according to the specific experimental

condition, and it could induce phase separations (Haraguchi *et al* 1998b). In the interfacial region between silica and MPR–AA matrix of our material, a strong interaction is observed due to the attachment of the carboxyl groups to the silanol moieties that leads to a material with a remarkable optical transparency, a property that is not easily attained in the case of conventional composite materials.

Figure 2 shows a series of TGA thermographs related to SiO_2 /MPR–AA hybrid, SiO_2 and MPR–AA compounds. It is evident from this plot that the presence of silica improves thermal stability of the hybrid. The weight loss curves for the hybrid material show a two-step degradation mechanism; there exists first a continuous weight loss up to $\sim 650^\circ\text{C}$, followed by a less intense decomposition pace up to 1000°C . By comparing these two thermal spectra with TGA

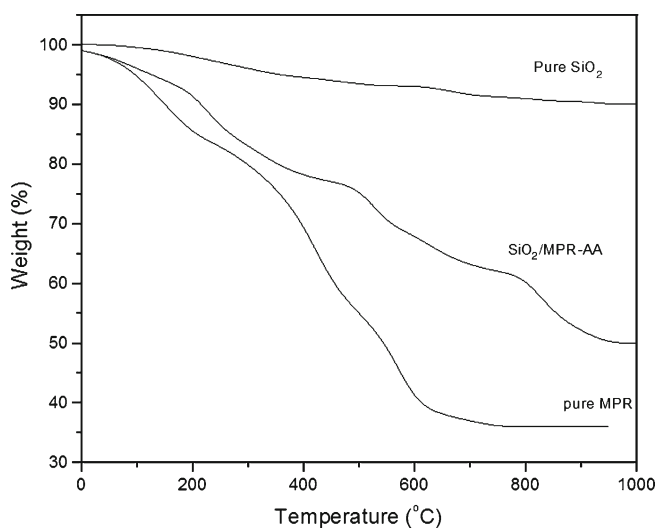


Figure 2. TGA thermal analysis of pure MPR, SiO_2 /MPR–AA hybrid material and pure silica.

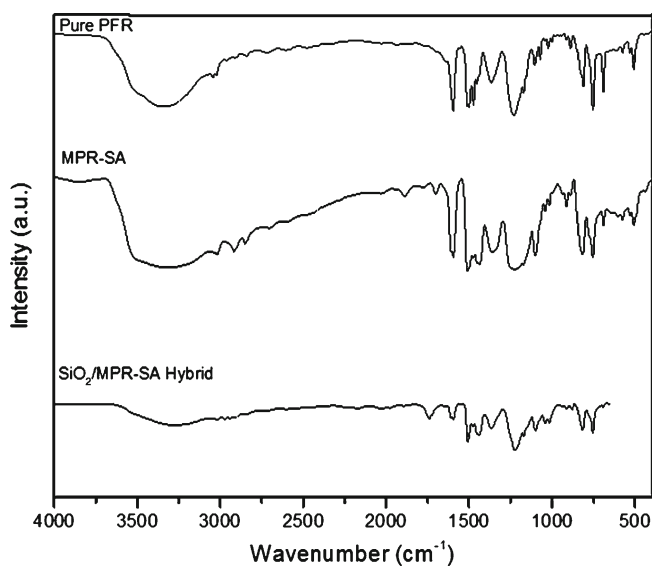


Figure 4. FT-IR spectra of pure PFR, MPR–SA and SiO_2 /MPR–SA hybrid material.

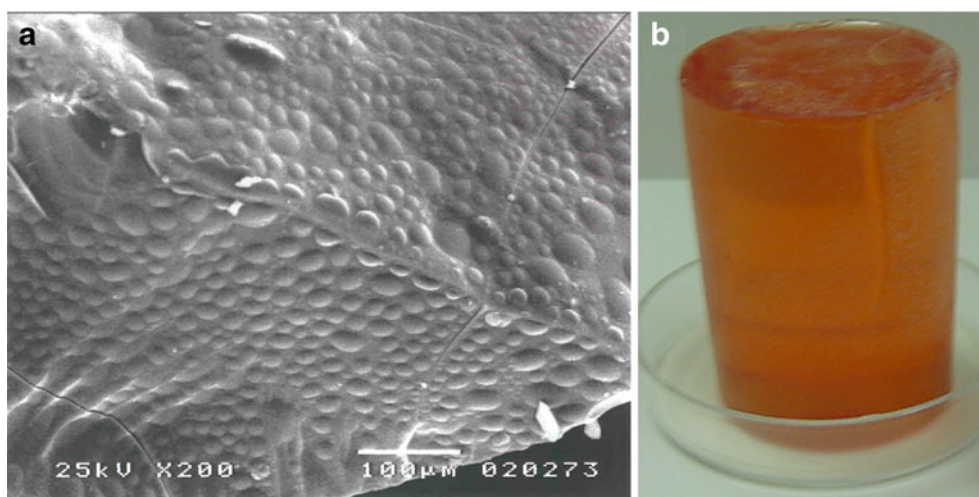


Figure 3. (a) SEM micrographs of SiO_2 /MPR–AA hybrid material at $200\times$ and (b) photograph of SiO_2 /MPR–AA hybrid.

thermograph of pure MPR-AA, it can be seen that the presence of SiO_2 does not influence strongly the rate of degradation of these hybrid materials in relation to pure MPR-AA.

SEM micrograph of the SiO_2 /MPR-AA hybrid is shown in figure 3(a) at $200\times$ magnification. In this micrograph, it is possible to observe a homogeneous distribution of the hybrid material, where silica particles are embedded within the resin matrix (MPR-AA). The size distribution is narrow, of around $10\text{--}20\text{ }\mu\text{m}$ and constituted by quasi-spherical particles. In figure 3(b), it is possible to see this material to be very homogeneous and translucent.

FT-IR spectroscopy results for the samples are summarized in figure 4. The spectrum of MPR-SA confirms functionalization of the Novolac-type resin with carboxylic groups, due to the presence of bands at 1703 cm^{-1} ($\text{C}=\text{O}$)

and at 1251 cm^{-1} ; the latter signal being attributed to the $\text{C}-\text{O}-\text{C}$ ester group vibration. In the spectrum of SiO_2 /MPR-SA, the ester carbonyl signals at 1740 cm^{-1} are evidence of the reaction between CO species proceeding from the carbonyl groups of MPR-SA and OH groups from the surface silanol groups. This is favoured by the electronegativity of oxygen and the readily available lone pair of electrons in the carbonyl group. Due to the nature of SiOH group, the polymer chain of PFR can be bonded by oxygen of the silanol groups (Panitz and Wokaun 1997). The bands corresponding to Si-O-Si symmetric and asymmetric vibrations are located at 754 and 1099 cm^{-1} , respectively. Because the reaction was favoured by the high electronegativity of oxygen and by the acidic nature of SiOH groups (Greenler 1962), the polymer end chains of MPR-SA were bonded to silanol groups on the surface of the SiO_2 nanoparticles.

The results of DSC analysis pointed to a thermal stability for PFR up to 140°C , while the SiO_2 /MPR-SA hybrid indicated stability up to 210°C . The resulting glass transition temperature was 150°C for the SiO_2 /MPR-SA hybrid material (figure 5).

From SEM studies at $3500\times$ magnification (figure 6(a)), the presence of stearic acid on the surface of SiO_2 /MPR-SA hybrid results in an anisotropic structure, consisting of a network of fibre-like features, and it is also possible to observe a homogeneous distribution of the hybrid material as shown in figure 6(b).

Figure 7 shows characteristics of the surfaces of Cu plates after being exposed to the saline chamber corrosion test for 72 h. A visual inspection of the coated Cu plates after corrosion tests revealed advantage of the presence of silica nanoparticles within the MPR matrix. This is seen on comparing figure 7(a) with 7(b-d). The former corresponds to the original resin, which already shows some corrosive attack as shown in figure 7(a) for MPR-AA and figure 7(c) for MPR-SA, whereas the coating remains unaltered by the corrosion test. The SiO_2 /MPR-AA hybrid in figure 7(b) and

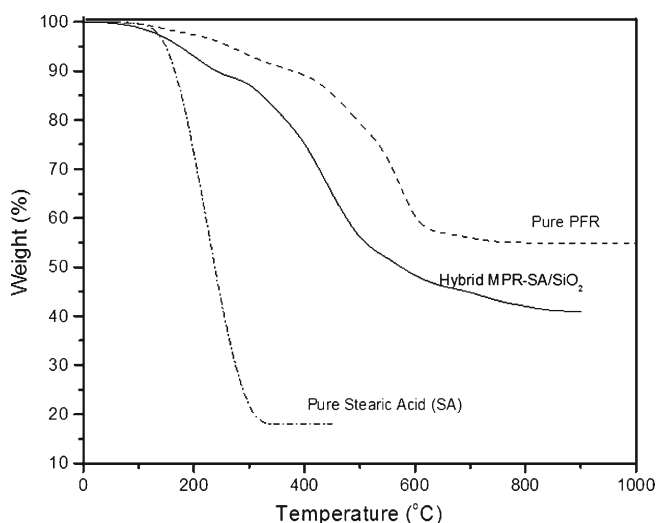


Figure 5. DSC thermal analysis of pure PFR, SiO_2 /MPR-SA hybrid material and pure stearic acid.

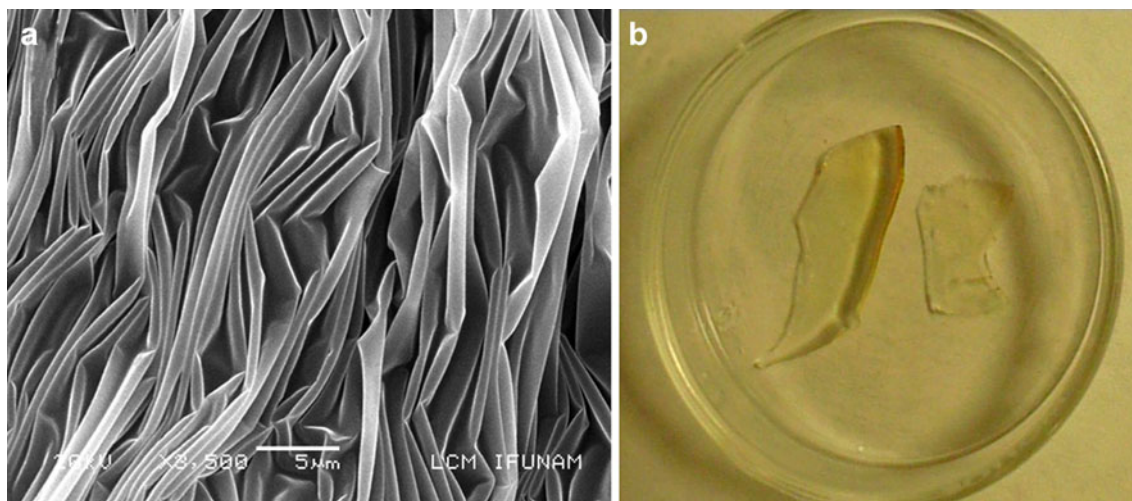


Figure 6. (a) SEM micrographs of SiO_2 /MPR-SA hybrid material at $3500\times$ and (b) photograph of SiO_2 /MPR-SA hybrid.

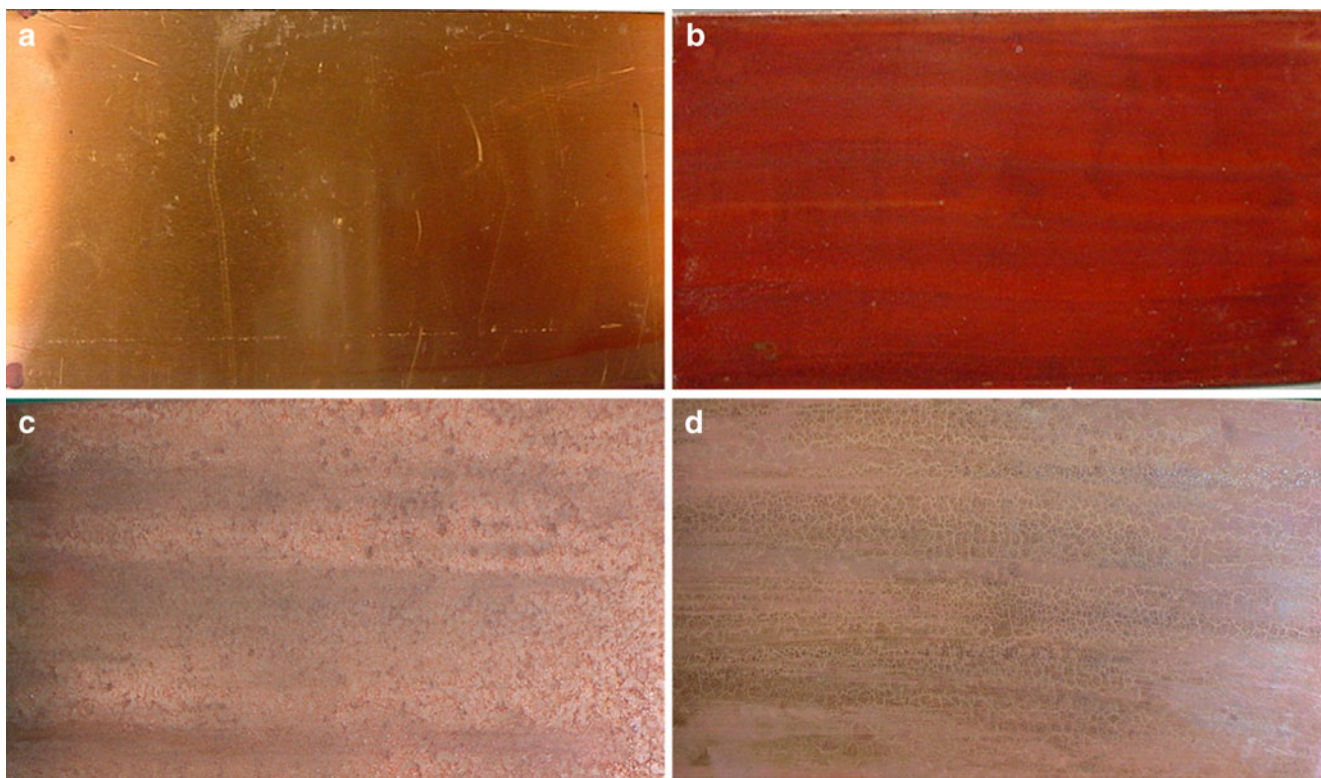


Figure 7. Photographs of Cu plates after 72 h coated with: (a) MPR-AA, (b) SiO₂/MPR-AA hybrid, (c) MPR-SA and (d) SiO₂/MPR-SA hybrid.

the SiO₂/MPR-SA hybrid in figure 7(d) are sensibly less affected by the saline mist.

4. Conclusions

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 resin (SiO₂-MPR). FT-IR spectroscopy of the resulting hybrid materials showed that the silica species was chemically bonded, thus suggesting that the interaction between these two components in the hybrid was due to hydrogen bonding between the silanol and the phenolic carboxylic hydroxyl groups (or phenolic hydroxylic groups). On the other hand, the interface appearance observed by SEM, leads to view these hybrid materials as potentially relevant for future technological developments, since the control of nanoscale morphology, especially monolithic glass, is the key to model and design engineering materials. The characterization of the above substrates through various techniques, including corrosion tests, demonstrated a superior performance of these innovative hybrid materials.

Further studies on the microstructures, as a function of other physical and chemical characteristics, along with full mechanical characterization, are currently under way. The presence of resin controls crystal growth influencing the

transparency and dispersion, thus reducing aggregation and agglomeration. Finally, we can say that the combination of silica and MPR resin matrices by the method herein described, allows enhancing the stability of the material, resulting in a glassy hybrid ceramic-like material with unique properties, still to be studied in detail with different polymeric systems.

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