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Hybrid ceramic-polymer coating used to protect metallic surfaces against corrosion

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HYBRID CERAMIC-POLYMER COATING USED TO PROTECT METALLIC SURFACES AGAINST CORROSION

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A new hybrid ceramic-polymer coating was designed to provide a chemical barrier to protect metallic substrates against corrosion. This material is completely hydrophobic, protecting the coated surface from chemical attack from its environment. A good adhesion between the organic and inorganic phases was achieved, producing a high-performance coating, with the additional advantage of having a good wear resistance, high transparency and excellent resistance to UV radiation.

Keywords: hybrid material, ceramic-polymer coating, anti-corrosive, anti-abrasive, silica particles, poly(methylmethacrylate), Optical transparency

1. INTRODUCTION

One of the newest trends in the design of high engineering materials is the use of hybrid materials that combine in a single one the properties of organic and inorganic compounds [1]. This kind of material can be

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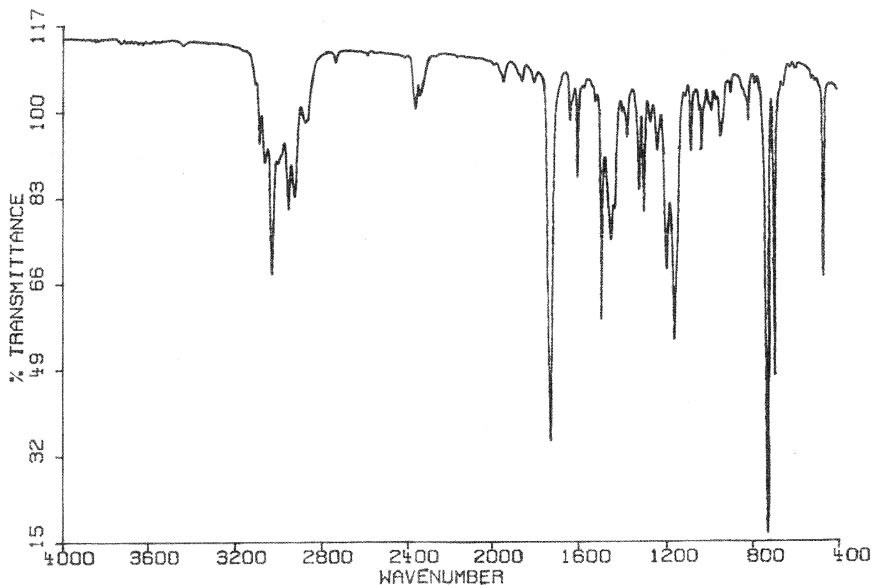
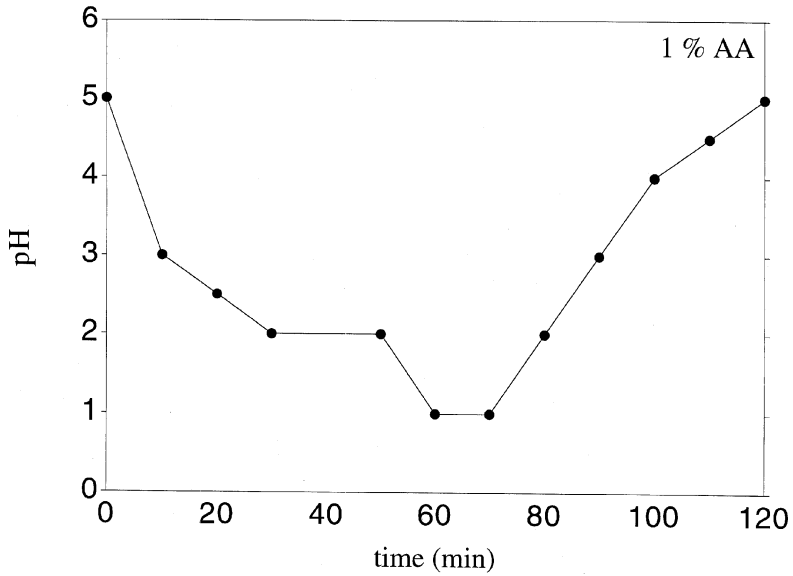


FIGURE 1 FT-IR spectrum of hybrid ceramic-polymer coating in toluene. The bands of the Si-Cl vibrations located in the range from 450 to 625 cm^{-1} was not observed, meaning that all the CA already reacted with the hydroxyls on the silica particles.

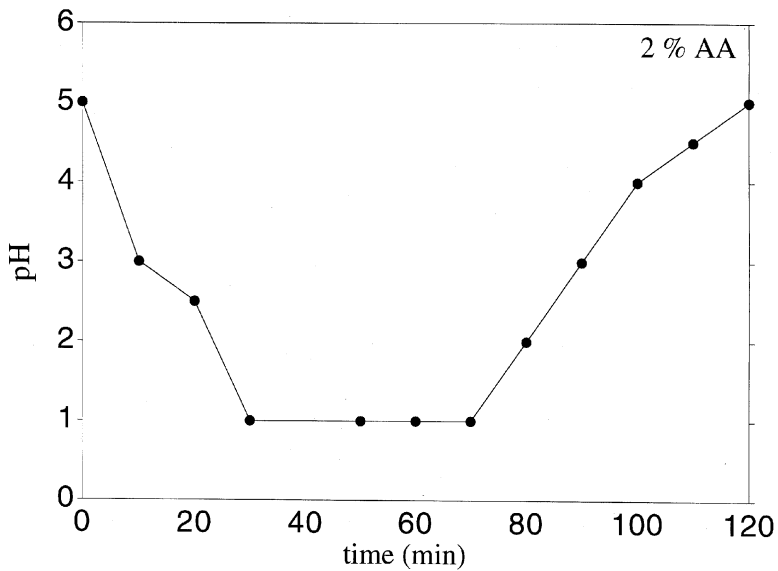
obtained by joining, in a single structure, ceramics and polymers; these are widely used in a large field of applications, including research and industry [2].

Many of the high engineering materials fulfill the main requirements imposed on them. However, when an additional requirement is also imposed, like high transparency, good adhesion with the substrate, high abrasion resistance, etc., these materials may fail in their performance. In these cases, hybrid materials play an important role because the properties of the ceramic and the polymer, generally complementary, are added synergistically to produce a new material with very interesting properties [3,4].

Some important effort has been devoted, from a long time ago, to protect metallic surfaces to prevent corrosion. Corrosion is the main reason of failure of metallic structures. The amount of money spent to prevent and to repair structures attacked by corrosion is tremendous. In addition to the economic problem is the social aspect, because the cost in human lives is high [5,6].



(a)



(b)

FIGURE 2 Dependence of the pH with the reaction time during the functionalization reaction for: (a) 1% of CA and (b) 2% of CA.

To protect metallic structures against, corrosion, several techniques have been proposed. These protections range from the use of anti-corrosive oils, which have a limited applicability and not good performance, to paints, which offer only a physical barrier against corrosion. In the last case, differences in expansion coefficients, existence of stresses and deformations, lack of adhesion with the substrate, etc., can break or damage the polymeric coating, allowing the corrosive agents to attack the metallic surface; in this case the protection may become a corrosive chamber enhancing these effects [7,8].

In the present work, a hybrid coating made of ceramic nano-particles and polymer was produced. This material is completely hydrophobic forming not a physical barrier but a chemical barrier that produces repulsive molecular forces against the corrosive agents, avoiding the flux of these agents passing through the protective coating. This kind of protection is significantly more effective than the usual methods to avoid corrosion [4,9]. Additionally, the hybrid character of this coating make it highly resistant to wear.

2. EXPERIMENTAL

2.1. Polymer Synthesis

The polymer was synthesized by free radical polymerization using freshly distilled methylmethacrylate, industrial grade (supplied by Industrias Resistol, Mexico) and toluene (Baker Co.) as a reaction medium. The initiator was 2,2'-AzobisIsoButyroNitrile (AIBN) (Industrias Resistol, Mexico), in an appropriate concentration to produce poly(methylmethacrylate) (PMMA) with different molecular weights: 400,000, 500,000 and 700,000 g/mol. The polymerization was carried out at 80°C under strong agitation.

2.2. Ceramic Functionalization

Silica particles of 18 manometers (Degussa Co.) were chemically functionalized by using dichlorodimethylsilane (Aldrich Chem. Co.); this compound was used as the coupling agent (CA) between the ceramic phase and the organic polymer. A suspension of 30 grams silica particles in 100 ml toluene was prepared with a concentration of 30% wt. 0.5 ml solution of the CA in toluene at 2% wt. was added dropwise to the suspension with strong agitation; this mixture was heated to reach reflux conditions and stirred for 2 hrs.

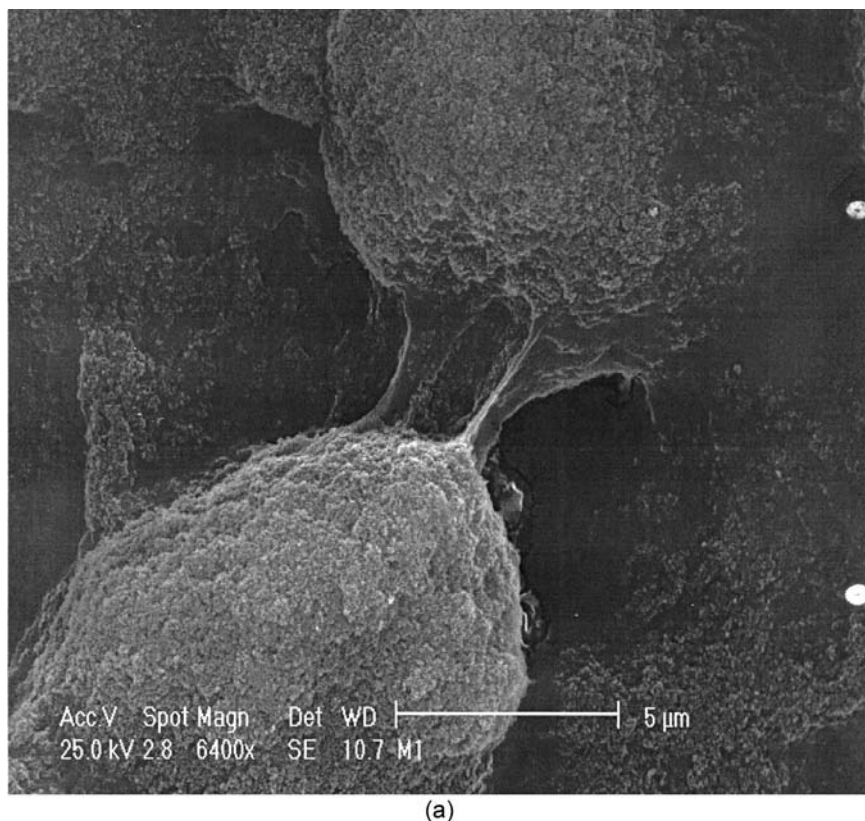


FIGURE 3 SEM micrographs of the hybrid coating. (*Continued*).

2.3. Hybrid Coating

It is known that pure silica nano-particles do not disperse well in toluene. However, when these are chemically functionalized, the methylsilane groups on the surface make the particles more hydrophobic, producing a good dispersion in toluene. Then, a mixture of functionalized silica particles in toluene produces a homogeneous and transparent dispersion [9].

37.4 ml PMMA solution also in toluene at a concentration of 40% wt. of solids was mixed, at room temperature and with strong agitation, with 17.4 ml of the dispersion of functionalized silica nano-particles during 20 minutes. A clear dispersion was finally obtained of a hybrid ceramic-polymer coating. This coating was used to cover the surface of steel plates, previously cleaned to remove grease, dust and

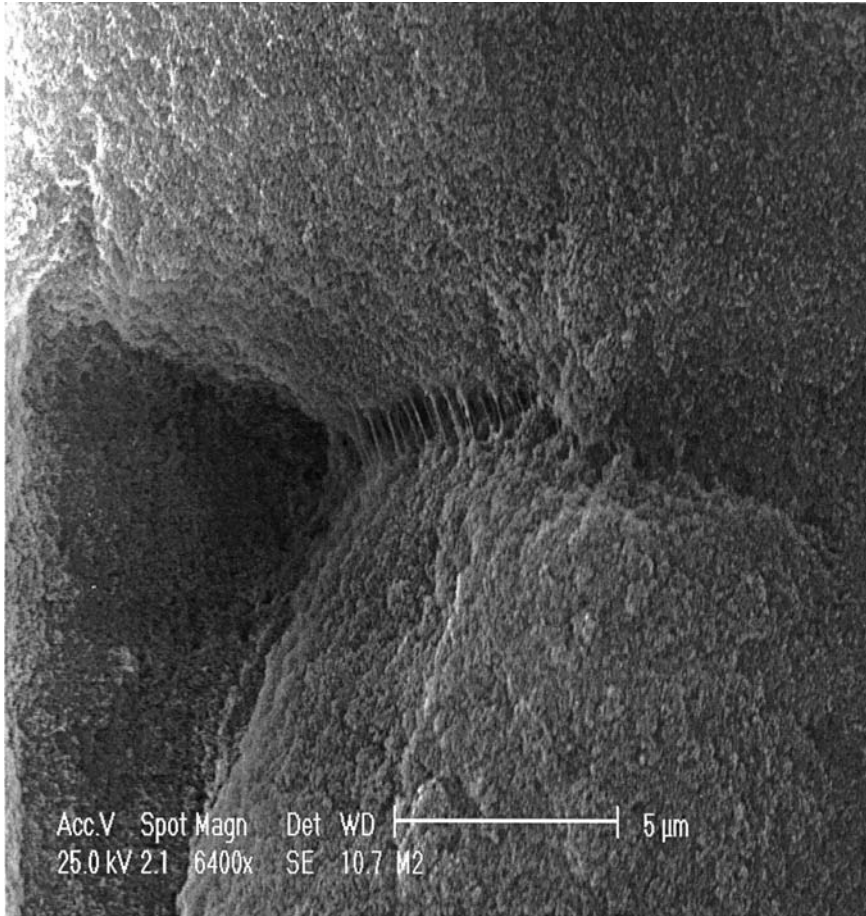


FIGURE 3 (Continued).

dirt particles. These metal plates were washed with Dextran and dried with acetone. The hybrid material was applied by using different ways: immersion, spray, and brushing.

A measure of the optical transparency of the hybrid coating provides us with an indirect method to determine if the silica nano-particles were well functionalized: a transparent coating means that the silica particles were well distributed in the polymeric matrix and this is achieved only if they are chemically functionalized. The transparency of a coating of 120 microns thickness supported on a corning glass was determined in a turbidimeter resulting higher than 98.7%.

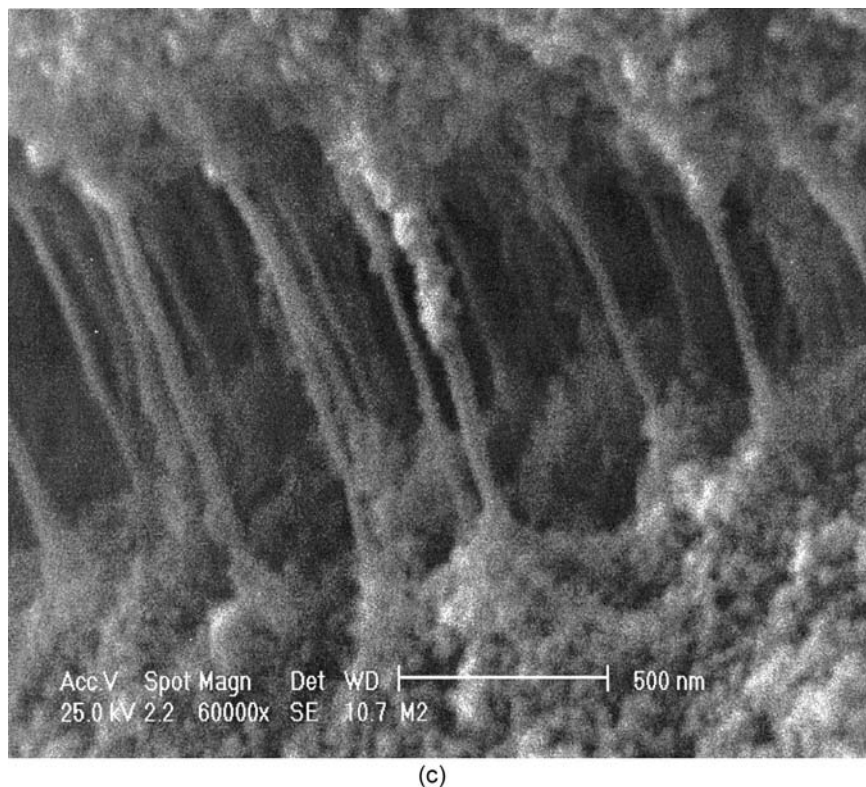


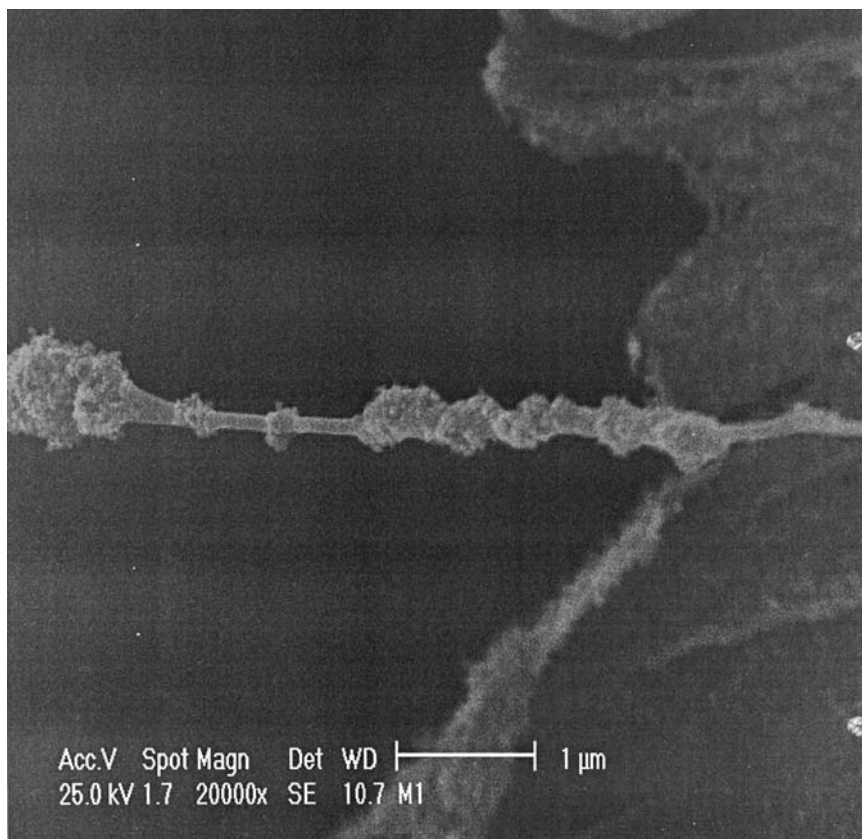
FIGURE 3 (Continued).

2.4. Electron Microscopy

Scanning Electron Microscopy (SEM) analysis was performed in a Phillips XL30 machine. The hybrid material was frozen with liquid N₂, broken and coated with gold by evaporation; the observation was made in the newly, formed surface. Metal plates covered with the hybrid material were also coated with gold for observation.

3. RESULTS AND DISCUSSION

A sample of hybrid coating in toluene was analyzed by FT-IR spectroscopy in order to detect the disappearance of the band corresponding to the Si-Cl bond. The disappearance of this band means that the CA indeed reacted with the silica particles. The functional group ≡Si-Cl has a stretching band of the Si-Cl bond at 470-550 cm⁻¹, while



(d)

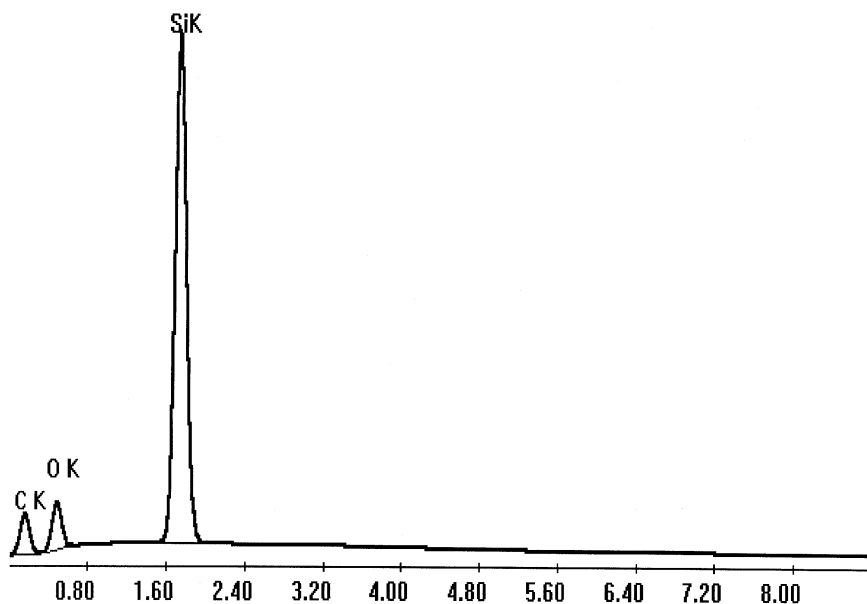
FIGURE 3 (Continued).

the group $=\text{Si-Cl}_2$ has an asymmetric stretching band of the Si-Cl bond at $535\text{-}595\text{ cm}^{-1}$ and a symmetric stretching band of the same bond at $460\text{-}540\text{ cm}^{-1}$. The FT-IR for the functionalized silica particles is shown in, Figure 1. As can be seen from this figure, no band in the range from 460 to 595 cm^{-1} was observed, meaning that the CA already reacted with the hydroxyls on the silica particles.

In this figure it is possible to observe bands at 464 , 623 , 692 , 725 and 816 cm^{-1} corresponding to out-of-plane and in-plane ring deformations of the solvent. The set of bands from 2874 to 3056 cm^{-1} also corresponds to a C-H stretching vibration of the aromatic rings.

The bands at 1328 , 1646 and 1726 cm^{-1} corresponds to symmetric (weak) and asymmetric (strong) stretching of CO_2 – vibration of the

Label A: POLIMERO M1(PARTICULA)



(e)

FIGURE 3 (Continued).

acrylic polymer. The strong band at 1726 cm^{-1} corresponds to the stretching deformation of the C=O group, and the strong band at 1498 cm^{-1} to the C-H stretching vibration of the methyl groups. The strong band at 1157 cm^{-1} is assigned to the C-O stretching vibration of the acrylic group.

The functionalization reaction of the silica particles, shown schematically in equation (1), can also be followed by measuring the pH as a function of the reaction time. In Figures 2a and 2b it is possible to see the variation of the pH versus the reaction time for a system with 1 and 2% wt. of the coupling agent, respectively. In the first stage of the reaction, the pH is reduced from 5 to 1 due to the formation of the HCl. After this, there is a steady state regime where the pH does not change appreciably with time, followed by an increment in pH due to the evaporation of the HCl; this is because the chemical reaction was

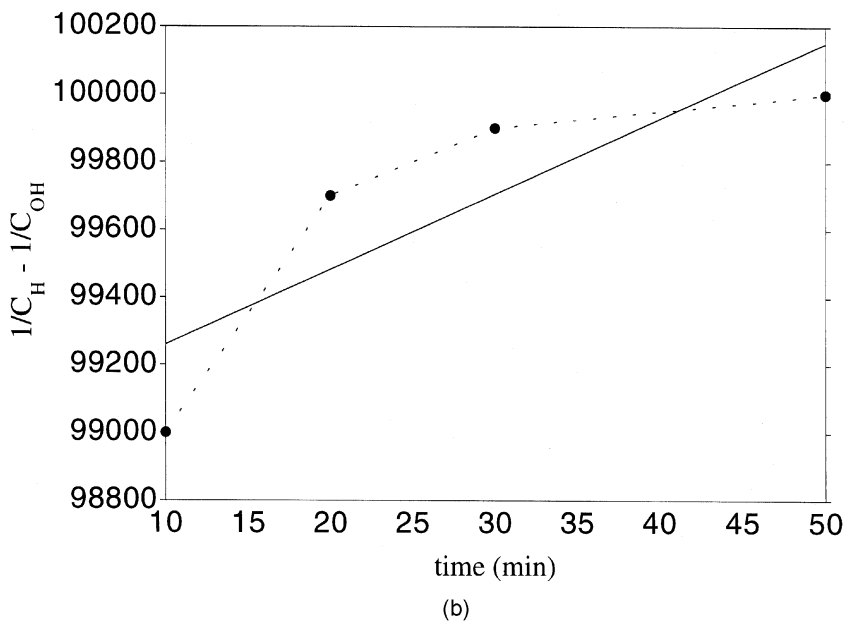
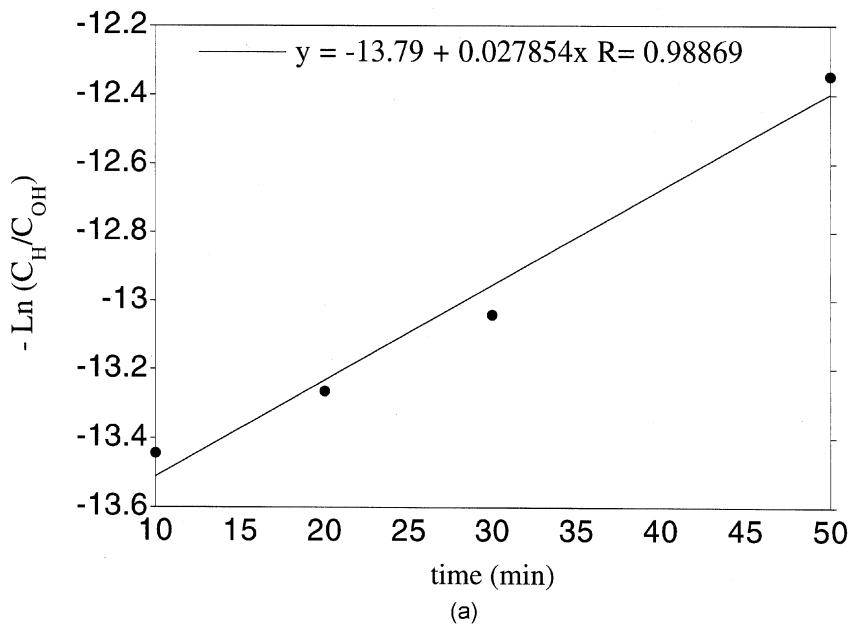
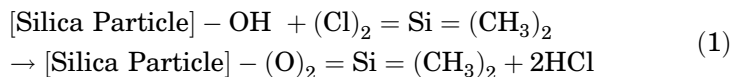


FIGURE 4 The order of the functionalization reaction was determined plotting: (a) $-\ln(C_H/C_{OH})$ and (b) $1/C_H - 1/C_{OH}$ versus the reaction time. The best fit was obtained for plot (a) corresponding to a kinetics of first order.

carried out in open conditions. Finally, the system recovers the initial pH value of 5.



Functionalized silica should be compatible with organic polymers; this means that the polymeric solution should wet the surface of the functionalized silica. In Figure 3a through 3d it is possible to see SEM micrographs of the hybrid material. In figs. 3a and 3b it is possible to see silica particles fully covered with polymeric material forming a cluster; this means that the silica particles were well wetted by the organic phase; in Figure 3c it is possible to observe a detail of the region between the particles where single silica particles are fully covered with polymer forming a thread. In Figure 3d is also possible to see a thread of polymeric material where single silica particles are fully immersed in the polymer. In Figure 3e the EDS spectrum of the silica particles is shown; the chemical analysis corresponds to the following weight percentages: carbon 47%, silicon 30.17% and oxygen 30.2%.

The fact that the silica particles are fully covered by polymer is due to the presence of the coupling agent. The interface between the ceramic particles and the polymer gives the good properties to the hybrid material: high anti-corrosive protection and high abrasion resistance.

The order of the chemical reaction between the silica particles and the coupling agent in the functionalization process was determined. In Figure 4 it is possible to see the plots of $-\ln(C_H/C_{OH})$ and $1/C_H - 1/C_{OH}$ versus the reaction time. In both cases the continuous line corresponds to least square fitting of a straight line. As can be noticed, the best fit corresponds to a first order kinetics.

In Figure 5a and 5b it is possible to see pictures of steel plates uncovered and covered with the hybrid coating; the corrosion test was done in a saline chamber for 22 hr where a fog produced by an aqueous saline solution at 3.5% wt. of NaCl and at 35°C was employed. As can be noticed, the plate without coating shown in Fig. 5a was severely attacked by oxidation, while the one covered with the hybrid coating (Fig. 5b) was exceptionally well protected where no oxidation stain was observed on the surface.

The presence of inorganic phase in the hybrid material provides a good protection against wear; because the ceramic particles more

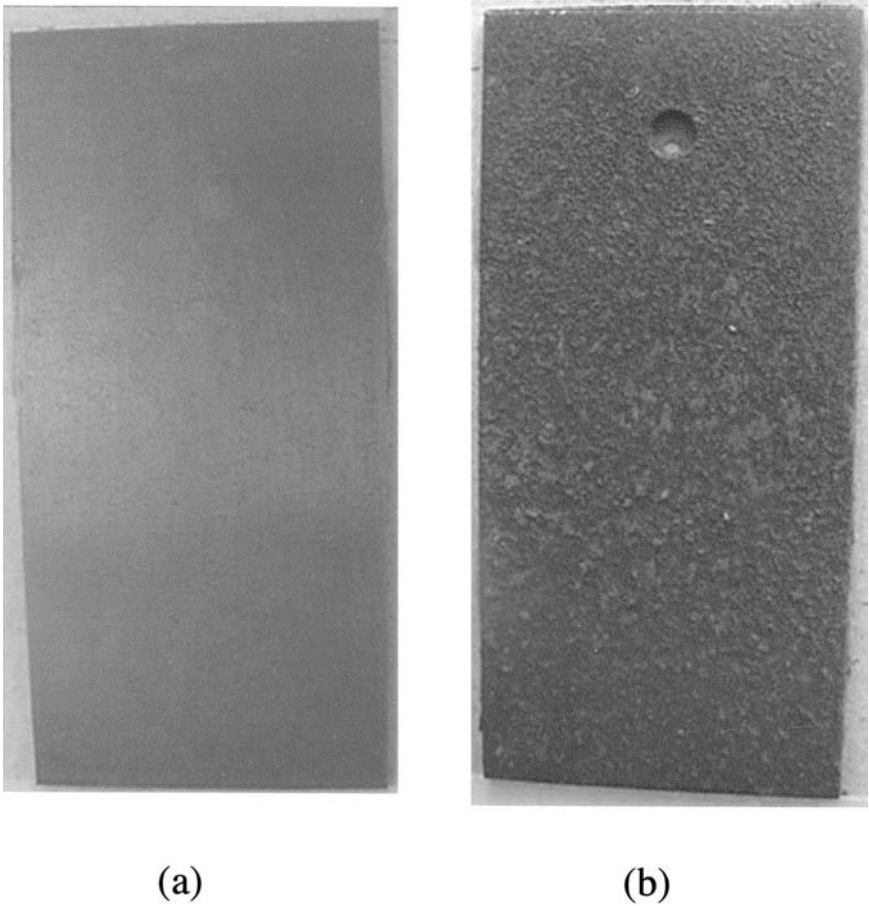


FIGURE 5 Pictures of metal plates (a) with and (b) without the hybrid coating.

rigid and wear resistant than polymers, this hybrid coating has a considerably high abrasion resistance. As can be noticed in Figure 6, where the weight loss is plotted as a function of the abrasion time, it is possible to significantly reduce the weight losses by using a hybrid coating. From this plot it is possible to see that the hybrid coating loses weight 400% slower than a coating without silica particles.

In Figure 7 some preliminary results of the corrosion rate are reported. In this figure it is possible to observe the corrosion rate in

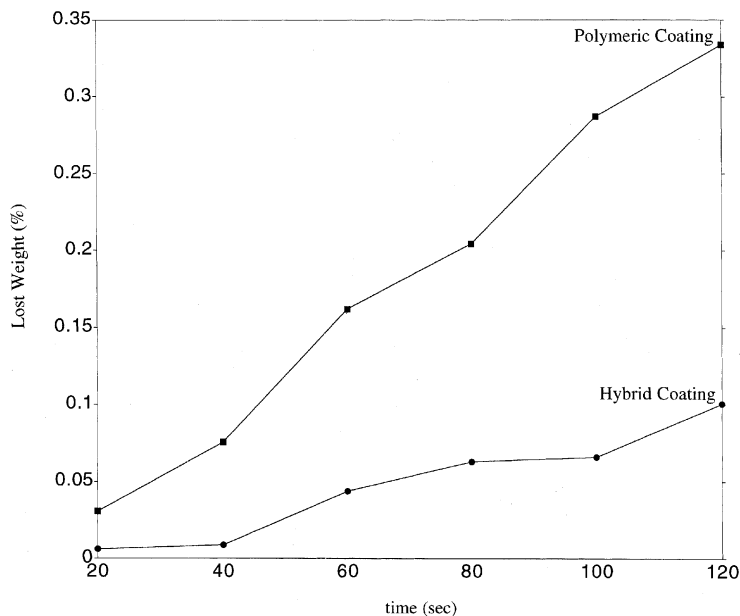


FIGURE 6 Weight loss of the hybrid coating as a function of the wearing time.

mm/year corresponding to steel plates coated with the hybrid material at two different ceramic concentrations: the curve (a) corresponds to a ceramic:polymer ratio of 30:70, while the curve (b) to a composition of 70:30. This test was carried out placing the coated plates in a corrosive medium of $\text{H}_2\text{O-NaCl}$ (3.5% mol) at 24°C for 26.7 hr. As can be noticed, the corrosion rate is lower for the system containing 30% ceramic but, for longer times, both systems have approximately the same corrosion rate. The corrosion rate for the reference (without coating) is not shown because it is much larger than the other two.

4. CONCLUSIONS

A new coating ceramic-polymer material was produced by using a coupling agent to modify the surface of the silica nano-particles. With this procedure it was possible to have a good dispersion of these particles in a solution of PMMA in toluene. Because the silica particles have a size well below the wavelength of visible light, the hybrid

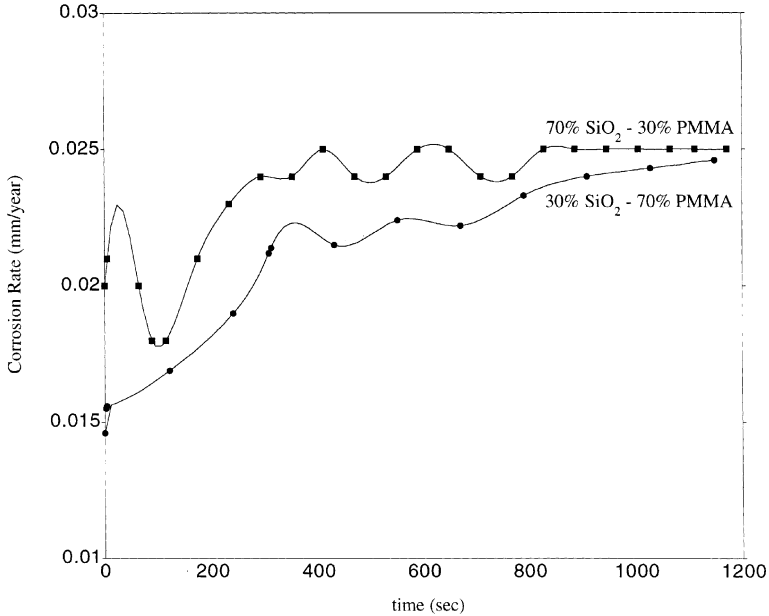


FIGURE 7 Corrosion rate for steel plates coated with the hybrid ceramic-polymer coating containing two different amounts of silica particles: (a) 30% and (b) 70%.

material is transparent. The hybrid coating protects effectively against corrosion and has an excellent wear resistance.

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