DEVELOPMENT AND CHARACTERIZATION OF CHITOSAN HYBRID COATINGS BY SOL-GEL METHOD

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Abstract

This paper describes the preparation and characterization of hybrid coatings constituted by SiO_2, TiO_2 and chitosan in varying compositions on aluminium, and glass substrates by sol–gel method. The optimized sol-gel solutions were deposited using by dip-coating and spray coating and the thermal treatment conditions (temperature) were optimized. In particular, condensation reactions necessary to allow the formation of the metal oxide networks were performed by storing the films in an open-air oven at 100°C and 80 °C for 30 minutes. Moreover, the functionalization of hybrid has been carried out with vinyltrimethoxysilane (VTMS).

The films were investigated by scanning electron microscopy (SEM), Fourier transformed infrared (FTIR) spectroscopy, hydrolytic degradation, corrosion resistance and adhesion test.

The process yields transparent chitosan hybrid coatings with good adhesion on glass and aluminium substrates.

The obtained results suggest that the functionalization of the hybrid coatings was affected through in situ hydrolysis–condensation reaction of vinyltrimethoxysilane (VTMS) in the reaction medium.

Keywords: *sol-gel process, chitosan, hybrid, corrosion*

1. INTRODUCTION

The coatings are one of the most interesting alternatives in the protection and functionalization of several materials, such metals, glass and polymers. In this context, sol–gel coatings can offer many and well-known advantages, including relative low processing temperatures, homogeneity purity of the resultant materials preserving the bulk properties of substrates. Thus, this technique appears as competitive with other deposition techniques, due to its simplicity and less costly equipment.

The classical sol-gel process consists of a two-step hydrolysis-condensation reaction starting with metal alkoxides M(OR)x, typically tetraethoxysilane. The presence of an organic oligomer or polymer in the reactive system, bearing suitable functional groups that are reactive toward the other reactants of the sol-gel process, leads to the formation of covalent or hydrogen bonds between organic and inorganic components that are typically phase separated on a nanometric scale [1].

It is well known that the final morphology of these hybrid materials, and thus their physical properties, is strictly dependent on the characteristics of the organic polymer, such as its molecular weight and its solubility in the sol-gel solution, as well as the presence of reactive functionalities and their associated chemical reaction rates. Other parameters such as phase separation, solvent evaporation rate, and sample thickness also play an important role [2].

In the present work, we investigated the chemical and physical properties of organic-inorganic (O-I) hybrid coatings prepared with tetraethoxysilane (TEOS) as silica precursor and chitosan as organic component. Several works are available in the literature on the promising properties of silica-chitosan composites [3,4].

Silica is the most widely investigated inorganic component in the sol-gel process, and the compatibility of silica with various bone relevant proteins such as chitosan has already been demonstrated [5].

Chitosan is a copolymer of linked β(1 → 4), 2-amino 2-deoxy-D-glucose, and 2-acetamidodeoxy-D-glucan prepared by alkaline deacetylation of chitin, commonly found in shells of marine crustaceans and cell wall of fungi [6]. Since chitosan exhibits high antimicrobial activity against pathogenic and spoilage micro-organisms, including fungi, is mainly used in the medical, pharmaceutical, cosmetics, and food industries [7]. Moreover, the studies concerning protection of metals using siloxane-based films have consistently demonstrated that siloxanes, could efficiently protect metals against different forms of corrosion. For example, M. Kalaiyarasan et al. prepared chitosan/silica hybrid to enhance the biocompatibility and corrosion resistance of biodegradable AZ31 Mg alloy [8]. Then, various formulations of sol-gel hybrids coatings loaded with chitosan showed to have good adhesion to titanium substrates and also antibacterial properties [9].

The use of organically modified silane precursors for the silica can impart enhanced properties to the hybrid. S. Smitha et al. investigated the preparation of new organic–inorganic hybrid synthesized through a sol-gel process starting from TEOS and methyltrimethoxysilane (MTMS) and vinyltrimethoxysilane (VTMS) have been added as coupling agents in the reaction medium. The process yields highly transparent and hydrophobic silica–chitosan hybrid.

To summarize, we prepared various formulations of chitosan hybrid coatings for of aluminium and glass substrates. We studied the incorporation of chitosan molecule in the network and examined the effect of the film composition on various important properties, such as the hydrolytic degradation, corrosion resistance, and chemical and morphological properties have been studied.

2. MATERIALS AND METHODS

2.1. Materials

The chemicals employed in the preparation of conversion coating are chitosan (Oxford, Vitality), glacial acetic acid (Alfa Aesar >99.9%), acetone (Sigma Aldrich) and ethanol (Sigma Aldrich). The sol was synthesized from the silica precursor using tetraethyl orthosilicate (TEOS, Sigma Aldrich >99.9%) and vinyltrimethoxysilane (98% VTMS, Aldrich). Tetraethyl orthotitanate (TEOT, Aldrich >95%) was used as titania precursor. The sols were applied onto different substrates depending on the characterization method used.

To obtain free films for the chemical characterization of each material, 3 ml of each sol was dropped into a non-stick teflon surface.

To determine the corrosion resistance of the coatings, bright finish commercial grade aluminum plates (25 mm x 25 mm) both polished and unpolished were used as substrates. The polished ones were grinded with SiC paper down to 1200 grit and polished with diamond suspension (1 μm) and before coating, as the untreated plates, were cleaned with ethanol and air dried. Microscope glass slides (2.5 × 7.6 cm^2) were used as substrates to verify the coatings transparency.

2.2. Preparation of coatings

In a typical experiment, silica sol was prepared by mixing 2 g TEOS with 7.9 g ethanol. The stirring was continued for 2 h at 30 °C. Chitosan (1 g) was dissolved in 2% acetic acid (aqueous) under stirring. Titania sol was prepared by dissolving 0.5 g of TEOT in 7.9 g acetone We synthesized several types of coatings, the content of chitosan in these materials varied from 0% to 50% (wt/wt) of the precursors weight. The compositions of these formulations are shown in table 1. The solution was prepared by dissolving TEOS in ethanol, then Chitosan solution was added to silica sol under constant stirring. Stirring was continued for 10 min, and VTMS was added to this mixture. Then, the stirring was continued for 10 minutes at 60°C.

The application of sols was performed by dip-coating and by air-brushing [10]. These deposition techniques were chosen, on a laboratory scale, taking into account the industrial applicability and the possible technological solutions necessary to implement these surface treatments in the industrial traditional process. During the airbrushing application, the substrates were kept at a distance of about 14 cm from the air-brush applicator. Each sample was coated with 0.1 ml/cm^2 of solution. After coating,

the surfaces were air-dried at room temperature for 2 hours and finally heat-treated at 80°C and 100°C for 30 min (see Fig.1).

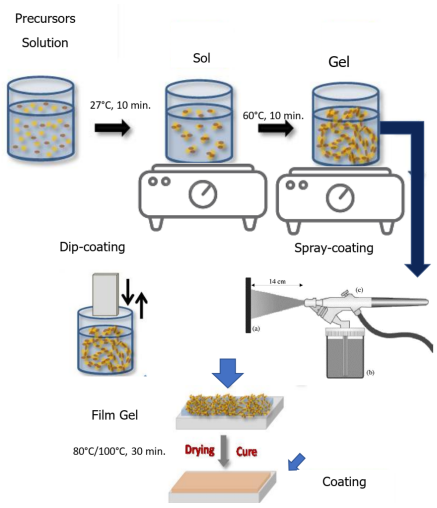

Fig. 1. Model of organic-inorganic coatings preparation by sol-gel process.

Sample ID	Chitosan (wt.%)	TEOS (wt.%)	TEOT (wt.%)	VTMS (wt.%)
0C100S	0	100	0	0
50C50S	50	50	0	0
50C50S*	50	50	0	0.01
75C25S*	25	75	0	0.01
50C45S5T	50	45	5	0.01

Table 1. Formulations nomenclature

2.3 Characterization

Structural characteristics of the hybrid were investigated using a IRAffinity-1S FTIR spectrometer (Shimazdu corporation) in the range of 600–4000 cm^{-1} to identify the presence of functional groups on the sample surface. Scanning electron microscopy (SEM) images were collected using a high-vacuum tungsten filament microscope (Hitachi mod 2300A, dedicated software: Thermo Noran NSS) with a working bias of 20 kV. To obtain high-resolution images, all samples were Sputter coated with Au-Pd alloy before SEM observations.

Optical absorptance of coatings on glass slide was measured by UV-VIS Agilent Cary 300 spectrophotometer.

Corrosion resistance was assessed in an aerated 3.5% NaCl solution by means of potentiodynamic method. A three-electrode electrochemical flat cell was used, having an Ag/AgCl reference electrode (3.5 M KCl) and a platinum grid as counterelectrode. The specimen surface area exposed to the electrolyte was 1 cm^2. The tests were carried out after 1-h delay, using a rate of 0.3 mV s^{-1}. The hydrolytic degradation test was performed after soaking the coatings (deposited on a glass substrate) in distilled water at 37°C for about 1 months. The degradation kinetics was evaluated by examining the weight of the coatings before and after soaking for different periods of time. After soaking, the samples were dried in an oven at 37°C for 24 h and then weighed.

3. RESULTS

3.1 Results of structural and morphological analyses

Figures 2(a), 2(b), 2(c) and 2(d) represent FTIR spectra of 50C50S* sample, SiO_2 from TEOS, 50C50S sample and chitosan powder respectively. The characteristic peaks of chitosan corresponding to amide I (=C=O) is at 1640 cm^{-1} and NH2 bending is at 1560 cm^{-1}. Antisymmetric stretching vibration of C-O-C bridge is present at 1150 cm^{-1} and skeletal vibrations involving C-O stretching are observed at 1070 and 1030 cm^{-1} [11]. All the spectra of hybrid coatings have bands associated with the vibration of siloxane bonds, Si-O-Si, around 1050 cm^{-1}, 960 $cm^{-1}$and 780 $cm^{-1.}$ The bands associated with the vibration of OH species (3300–3500 cm^{-1}), and Si-OH terminals (3740 cm^{-1}) appear overlapped with those of primary amines (3400–3300 cm^{-1}) and secondary amines formed after the reaction alcoxysilane – chitosan at 3350–3310 cm^{-1}. Signals ranging from 2870 and 2974 cm^{-1} belong to valence vibration of methyl- and ethyl- groups of TEOS and VTMS [12]. These bands are associated with aliphatic C–H stretching and they decrease after curing at 100°C.

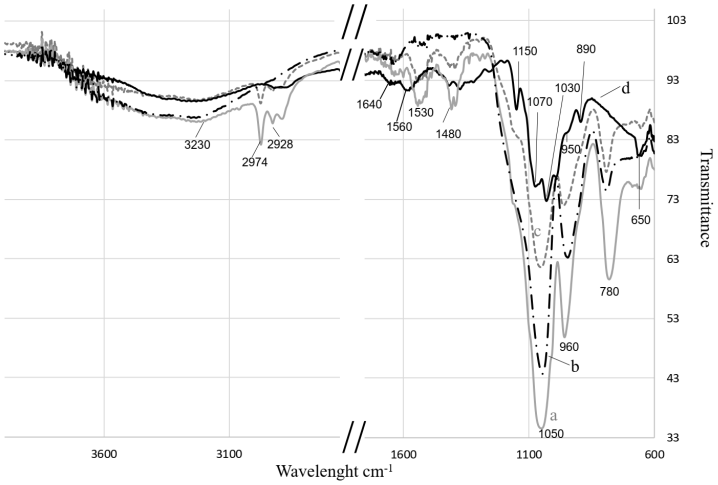

Fig. 2. FTIR spectra of (a) 50C50S* film (b) SiO_2 film from TEOS, (c) 50C50S film cured at 80°C and (d) chitosan powder.

In Fig. 3 and 4, SEM micrographs of the films formed on aluminium and glass substrates are shown. It was seen in SEM investigations that the films obtained from 50C50S* solution on glass and aluminium substrates has a smoothed and more uniform surface than the other films obtained by 50C50S and 50C45S5T formulations. The morphology of the 50C50S film on aluminium substrate (Fig. 3b) is not homogenous and high porosity and numerous micro-cavities can be observed. In the case of 50C45S5T (Figure 4a), the precursor solution contained 5wt.% of TEOT, formed heterogeneous film and cracked surface on the substrate. This is due to the higher condensation rate of rate of TEOT, leading to the agglomeration of the nano and submicroparticles and phase separation (see Fig. 4a).

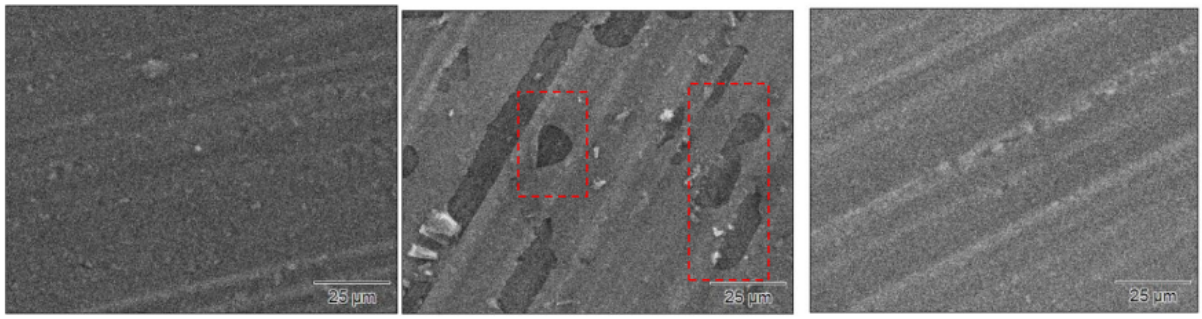

Fig. 3. SEM images at 1000 x of surfaces: a) aluminum substrate, b) 50C50S and c) 50C50S* coatings deposited on aluminum substrates by spray coating.

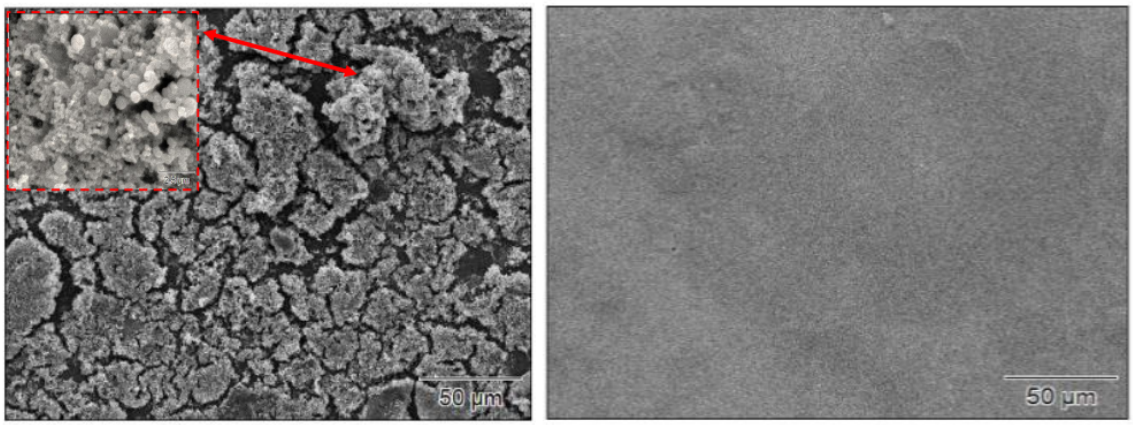

Fig. 4. SEM images at 500X of a) 50C45S5T and 50C50S* deposited by spray coating.

The optical properties of the surfaces prepared by 50C50S* solution and deposited by dip-coating and spray-coating were evaluated. All the prepared samples appeared defect-free to visual inspection. Moreover, the percent absorbance at 700 nm was used to characterize the appearance of films [13]. As showed in table 2, the optical absorptance of hybrid coatings on glass substrates was nearly 0%, and it is evident that the method of coating application in not an important parameter to control the final optical properties. It is also evident that there is not difference in terms of optical properties between the coatings prepared with and without VTMS (sample 50C50S* and 50C50S respectively).

Sample	Absorptance at λ = 700 nm (%)
Glass	0.3
50C50S* dip-coating	0.5
50C50S* spray coating	0.7
50C50S spray coating	0.6

Table 2. UV–visible absorptance measurements at λ = 700 nm (%)

3.2 Hydrolytic degradation

Polysiloxane network degrades in contact with water by hydrolysis involving the breaking of the network and therefore the elimination of the chitosan enclosed in it [14]. Figure 5 illustrates the weight lost after different periods of soaking, reflected by the corresponding degradation curves.

Degradation kinetics is faster for the film cured at 80°C (50C50S* sample) which experienced a higher hydrolytic degradation (64wt.%) after just 7 days. Considering Figure 5, the degradation kinetics of coating cured at 100°C is very slow, and after 27 days weight loss is of about 1 wt.%

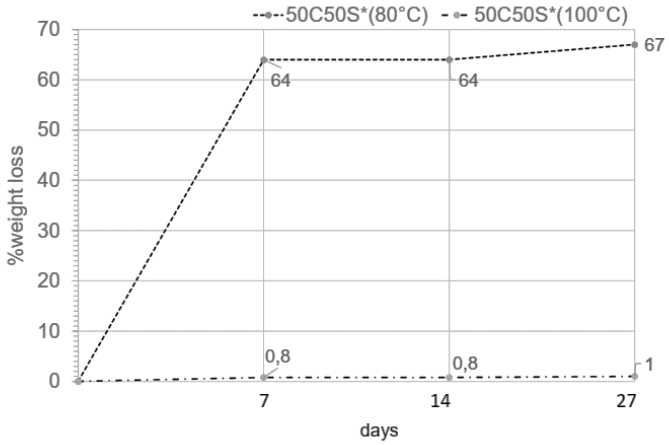

Fig. 5. Mass loss due to hydrolytic degradation of 50C50S* sample cured at 80°C and 100°C.

3.3 Corrosion resistance behaviour

The evaluation of corrosion resistance was carried out on aluminium substrates coated with 50C50S* film and cured at 100°C. Since delamination and adhesion of coating are crucial factors for corrosion mitigation, the study was conducted on aluminium before and after mirror polishing.

The results (Figure 6) show that the polished samples both untreated or coated showed an active behaviour, and the coating gave only a small increase of corrosion potential as compared to that of the untreated specimen.

The anodized untreated sample has a typical passive-transpassive behaviour, with fairly low anodic current density values in the passive branch. Higher corrosion potential and lower corrosion current values were observed for the coated aluminium unpolished indication, on the whole, a superior corrosion inhibition reasonably attributable to a stronger interaction of our hybrid coating with the unpolished substrate [15].

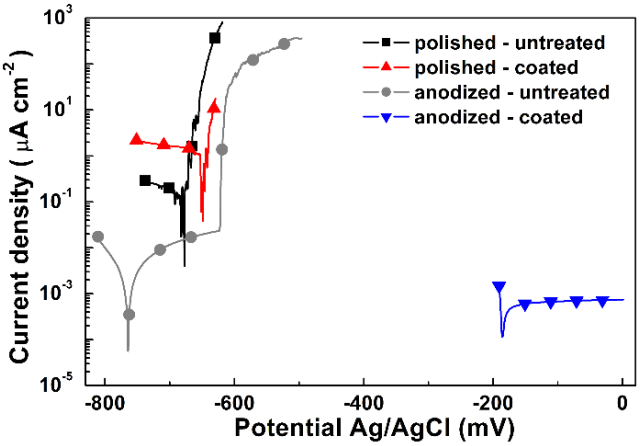

Fig. 6. Potentiodynamic curves in aerated 3.5% NaCl solution

4. DISCUSSION

All films silica-chitosan obtained by spray coating and dip-coating are transparent, indicating compatibility of the components at the molecular level.

The SEM analysis allowed an evaluation of the different morphology after the addition of VTMS in the solution underlining the homogeneous and best adhesion effect of VTMS on the coating.

While the addition of VTMS resulted in homogenous and smooth surface, the addition of TEOT in the solution, lead to heterogeneous film with high porosity and cracks. This kind of morphology result could be caused by the different reaction rate of the inorganic precursors to form the metal oxides, thus to titania's great propensity to crystallize and produce distinct phases [16].

The results of the degradation study test showed that the silica-chitosan coating cured at 80°C had higher degradation rates than the film cured at 100°C. This can be attributed to the lower degree of crosslinking as showed by the residual methyl- and ethyl groups in FTIR analysis.

Optical absorptance of hybrid coatings on glass substrates was nearly 0%, which makes the hybrid coating 50C50S* suitable for possible optical applications and also for preparation of transparent coatings on aluminum substrates.

The improved corrosion resistance displayed by the coated samples is attributable to the good affinity between the hybrid coating 50C50S* and aluminium substrate which enhance the stability of natural formed oxide layer in wet saline environment.

5. CONCLUSIONS

A chitosan–silica-based coating, obtained by sol–gel technique, was used in this work for glass and aluminium substrates. This study investigated the effect of several thermal treatments and VTMS presence, mainly the morphology, transparency degradation and corrosion resistance. The results showed that, with the proper thermal treatment, good degradation resistance can be obtained. The best surface properties are found after thermal treatment at 100°C and after the addition of VTMS. The coatings are transparent and crack-free.

A potential shift towards more positive values was recorded by potentiodynamic polarization measurements, showing an enhanced corrosion resistance provided by the 50C50S* hybrid coating.

On the base of the obtained preliminary results, chitosan-silica coating, seems to be highly promising as a novel sustainable film maker for packaging industry.

A wider analysis including different compositions and antibacterial test must be realized to have a complete assessment of coatings properties.

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