



Elaboration of SiO₂-PMMA-Nanoparticles of ZnO/TiO₂, Hybrid Coatings

Elaboración de Nanopartículas SiO₂-PMMA de ZnO/TiO₂, Recubrimientos Híbridos

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Abstract— SiO₂-PMMA-Nanoparticles of ZnO/TiO₂, organic-inorganic hybrid coatings were performed of a cross-linked polymethyl-methacrylate (PMMA) and silica was prepared via the sol-gel route using tetraethoxy-silane (TEOS) as precursor. 3-(Trimethoxysilyl) propyl methacrylate (TMSPM) was used to make compatible the organic and inorganic components of the precursor solution mixture. The hybrid coatings were deposited using precursor solutions with the reactants molar ratio 1:0.25 for TEOS: TMSPM, respectively, and using 0.25, 0.5, 0.75 and 1 of MMA molar ratio. Nanoparticles of 0.005 % molar ratio of ZnO/TiO₂ were embedded. Hybrid coatings were studied by UV/Visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FT-IR), atomic force microscopy (AFM) and thermogravimetric analysis (TGA). The hardness of the coatings was determined from a pencil hardness test referred to ASTM Standard D 3363-92. The AFM results showed that the hybrid coatings have a roughness of about pair of nanometers and consist of a homogeneous cross-linked organic-inorganic matrix with embedded nanoparticles of ZnO/TiO₂ very well dispersed. The hardness of the hybrid coatings was enhanced with respect to that of the pure organic component.

Keywords— Hybrid coatings, PMMA-Nanoparticles, ZnO, TiO₂

Resumen— SiO₂-PMMA-Nanopartículas de ZnO/TiO₂, se realizaron recubrimientos híbridos orgánicos-inorgánicos de un polimetilmetacrilato (PMMA) reticulado y la sílice mediante la ruta sol-gel utilizando tetraetoxisilano (TEOS) como precursor. Se usó metacrilato de 3-(trimetoxisilil) propilo (TMSPM) para hacer compatibles los componentes orgánicos e inorgánicos de la mezcla de solución precursora. Los recubrimientos híbridos se depositaron usando soluciones precursoras con una relación molar de reactivos de 1:0,25 para TEOS: TMSPM, respectivamente, y usando una relación molar de MMA de 0,25, 0,5, 0,75 y 1. Se embebieron nanopartículas con una relación molar de 0,005 % de ZnO/TiO₂. Los recubrimientos híbridos se estudiaron mediante espectroscopia UV/Visible (UV-Vis), espectroscopia infrarroja por transformada de Fourier (FT-IR), microscopía de fuerza atómica (AFM) y análisis termogravimétrico (TGA). La dureza de los recubrimientos se determinó a partir de una prueba de dureza con lápiz referida a la norma ASTM D 3363-92. Los resultados del AFM mostraron que los recubrimientos híbridos tienen una rugosidad de aproximadamente un par de nanómetros y consisten en una matriz orgánico-inorgánica reticulada homogénea con nanopartículas incrustadas de ZnO/TiO₂ muy bien dispersas. La dureza de los recubrimientos híbridos aumentó con respecto a la del componente orgánico puro.

Palabras Claves— Recubrimientos híbridos, Nanopartículas PMMA, ZnO, TiO₂

I. INTRODUCTION

Hybrid sol-gel derived materials are very versatile materials which combine the complementary properties of the inorganic and organic materials which constitute them [1-7]. The actual availability of a great number of precursors for the inorganic component through metal alkoxides, organo (alkoxi) silanes and nanoparticles and their compatibility to the incorporation of polymerizable groups such as methacryloxy, vinyl and epoxy groups, yield to the possibility to obtain a wide variety of hybrid sol-gel derived materials [1-4,7-15]. This type of materials are mainly used as coating for different purposes but recently also as bulk materials. They consist of a dual polymer network, in which cluster or polymer type inorganic structures are linked to organic groups or polymer fragments [1,10]. The hybrid networks can be conveniently divided in two general classes. Class I corresponds to hybrid systems, where organic molecules, oligomers, or low molecular weight organic polymers are simply embedded in an inorganic matrix. Both components exchange rather weak bonds, mainly through van der Waals, hydrogen, or ionic interactions. Class II corresponds to hybrid organic-inorganic compounds, where organic and inorganic components are bonded through stronger covalent or ionic-covalent chemical bonds [2,4,5]. Novel and multiple purpose hybrid materials can be obtained by choosing appropriately the inorganic and organic components with the adequate composition [2,4]. These materials have found technological applications in scratch and abrasion resistant coatings for plastics, corrosion protective coatings for metals, antistatic films, color decorative coatings for glasses and plastics, etc. [3,5,10,16-20].

Respect to inorganic sol-gel coatings, hybrid coatings provide also several advantages such as much better adhesion, transparency, flexibility and reduced surface roughness [21]. Actually, process as the coloration by dye hybrid coatings is applied in industrial processes to a variety of items such as crystal glasses, plastics, etc. [3,5,16-20].

In this paper, we have taken advantage in a hybrid organic inorganic polymethylmethacrylate-silica (PMMA-SiO₂) and nanoparticles of ZnO/TiO₂ matrix to obtain homogeneous, hard and high optical quality coatings on glass substrates. The coatings were prepared by the sol-gel method with a composition: 1:0.25 for TEOS: TMSPM, respectively, and using 0.25, 0.5, 0.75 and 1 of MMA molar ratio. Nanoparticles of 0.005 % molar ratio of ZnO/TiO₂ were embedded.

II. METHODOLOGY

Hybrid polymethylmethacrylate-silica coatings with 0.005 % molar ratio of ZnO/TiO₂ embedded were prepared using tetraethyl ortosilicate (TEOS, 99%, Aldrich), as the silica source, methyl methacrylate (MMA, 99%, Aldrich), 3-(trimethoxysilyl) propyl methacrylate (TMSPM, 98% Aldrich), ethanol (EtOH), as solvent, distilled deionised water, HCl as catalyst, ZnO nanoparticles (Aldrich), TiO₂ nanoparticles (Aldrich), benzoyl peroxide (BPO, Aldrich) as polymerization initiator. The precursor solution was prepared as follows: TMSPM was added to pre-polymerized TEOS solution of ethanol and then the substoichiometric amount of water (diluted HCl, pH 2) was added dropwise while stirring and then the solution was stirred at room temperature for 1 h. For the organic component, BPO was added to the MMA system and stirred at room temperature for 1 h. After that, both solutions were mixed. The precursor solution to deposit the hybrid coatings was prepared using molar ratio of reactants 1:0.25 for TEOS: TMSPM, respectively, and using 0.25, 0.5, 0.75 and 1 of MMA molar ratio. Nanoparticles of 0.005 % molar ratio of ZnO/TiO₂ were embedded. After that, the resulting solution was stirred at room temperature for 24 h. The hybrid coatings were deposited by the dip-coating method on pre-cleaned microscope glass slide substrates. All the obtained hybrid coatings were studied by Varian Cary 300 UV-Visible spectrometer in a range of 240 to 900 nm, Varian IR-640 FT-IR spectrometer in a range of 4000 to 400 cm⁻¹. Images of the coating surface were obtained by using an atomic force microscope Scanning Microprobe SPC 400 of Park Instruments. The thermal behavior was performed by TA Instruments SDT Q 600 in nitrogen atmosphere since ambient temperature to 900 Celsius degrees. The hardness of the coatings was estimated according to the pencil hardness test referred to ASTM Standard D 3363-92 [22].

III. RESULTS AND DISCUSSION

The UV-Vis spectra of the hybrid coatings (Fig. 1) showed that the coatings with TiO₂ absorb the UV radiation better than the other without, nevertheless, not exist a significant difference between the coatings with or without ZnO nanoparticles in all the spectra, but the coatings with TiO₂ has better optical properties of transmittance in the visible spectra range.

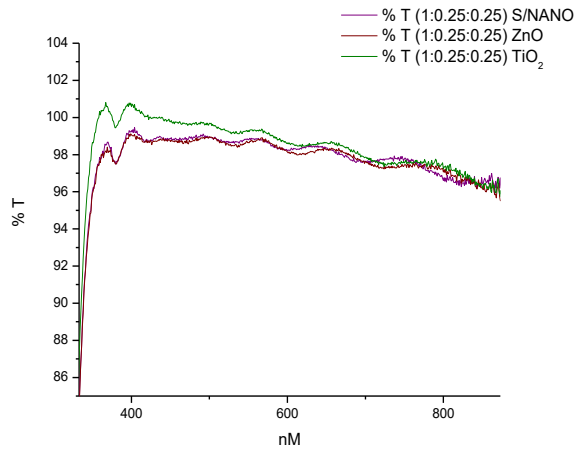


Fig. 1. UV-Vis spectra of (a) 1:0.25:0.25 without nanoparticles, (b) 1:0.25:0.25 with ZnO and (c) 1:0.25:0.25 with TiO₂, TEOS:TMSPM:PMMA molar ratio respectively.

In Fig. 1, the transparency window is due to % T spectra showing values above 95 % in the visible range. The interference oscillations, which are present, reveal the good optical quality of the coatings. The optical transparency of our hybrid coatings is another indication of their homogeneous composition of both organic and inorganic phases. This is because when both phases separate at macroscopic level in the hybrid matrix, the inorganic oxide phase scatters the light producing as the result opaque hybrid coatings. In order to analyze the experimental spectra of Fig. 1, an air/coating/substrate system was considered.

The infrared spectra of (a) 1:0.25:0.25 without nanoparticles, (b) 1:0.25:0.25 with ZnO and (c) 1:0.25:0.25 with TiO₂, TEOS:TMSPM:PMMA molar ratio respectively, hybrid coatings are shown in Fig. 2. The three spectra were normalized to the corresponding maximum value of the absorption and they are arbitrarily displaced along the absorption axis. The spectrum of the (a) 1:0.25:0.25 without nanoparticles is very similar to those of hybrid films reported in the literature [23-25]. It displays intense absorption peaks at about 954, 1080, 1170 cm⁻¹, and a broad band between 3100 and 3600 cm⁻¹, associated with the absorption of the Si-OH group, transversal optic (TO) Si-O-Si asymmetric stretching, longitudinal optic (LO) Si-O-Si asymmetric stretching and hydroxyl groups, respectively. In addition, it is observed a weak signal at about 800 cm⁻¹, which is related to the absorption by Si-O-Si symmetric stretching. The appearance of the first peak indicates an incomplete condensation of the Si-OH bond in the hybrid matrix and the peaks due to the Si-O-Si asymmetric and symmetric stretching evidences the formation of the silica network by the sol-gel process. The increasing of the second peak respect to the first one has been attributed to an increase in the porosity of the SiO₂ matrix [26]. It has been reported that the organic-inorganic interfacial interaction can be given through the formation of hydrogen bonds [23,24]. In our case, the residual silanol groups in the silica structure are capable to form hydrogen bond and their presence is evidenced in the hybrid coatings by the absorption peak at 954 cm⁻¹ and the broad absorption band due to the hydroxyl groups in the FT-IR spectra of two hybrid coatings with nanoparticles.

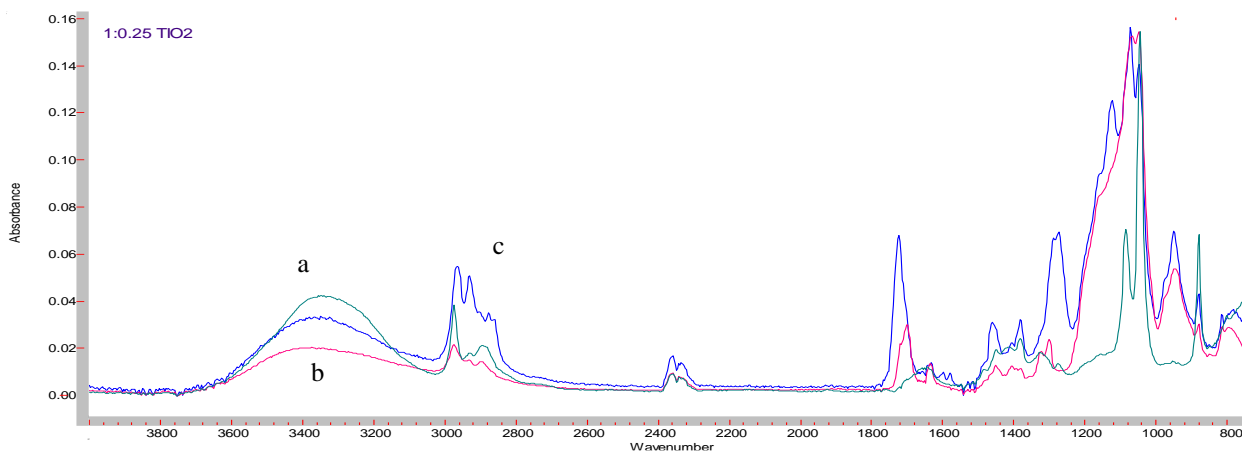


Fig. 2. Infrared spectra of (a) 1:0.25:0.25 without nanoparticles, (b) 1:0.25:0.25 with ZnO and (c) 1:0.25:0.25 with TiO₂, TEOS:TMSPM:PMMA molar ratio respectively.

Thus, infrared measurements are compatible with the formation of hybrid coatings with a homogeneous matrix constituted by both organic and inorganic components with embedded nanoparticles.

In Fig.3 (a), (b), (c) and (d) are shown 3-D AFM images taken from a 500 X 500nm area in the surface of the hybrid coatings. The morphology of the surface is very similar for (a) and (b) hybrid coatings; nevertheless, the difference between (c) and (d) is due to the presence of TiO₂. In all the cases, it is possible to identify the variation of concentration of PMMA, and when the coatings have TiO₂ nanoparticles; furthermore, all the coatings showed very smooth and flat surfaces with very low roughness.

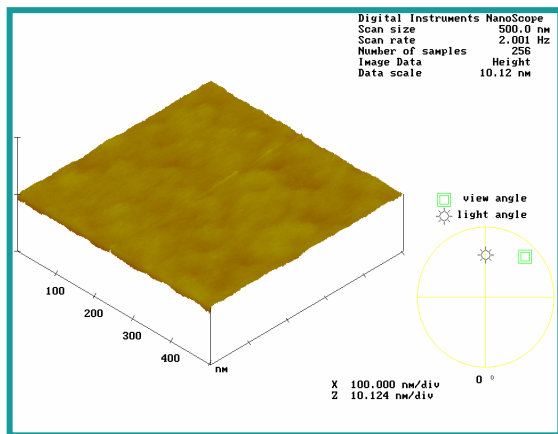


Fig. 3a. AFM of 1:0.25:1, respectively of TEOS:TMSPM:PMMA, without nanoparticles

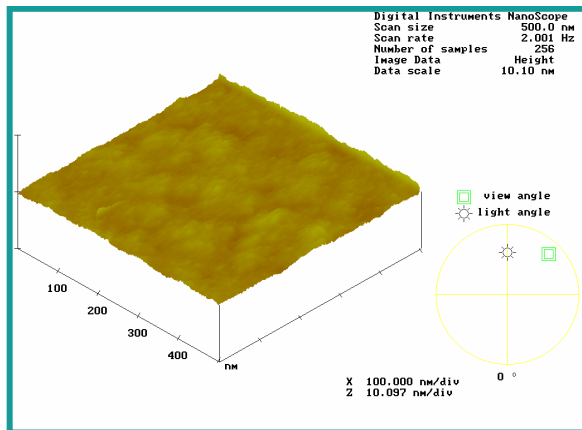


Fig. 3b. AFM of 1:0.25:1, respectively of TEOS:TMSPM:PMMA, with ZnO nanoparticles

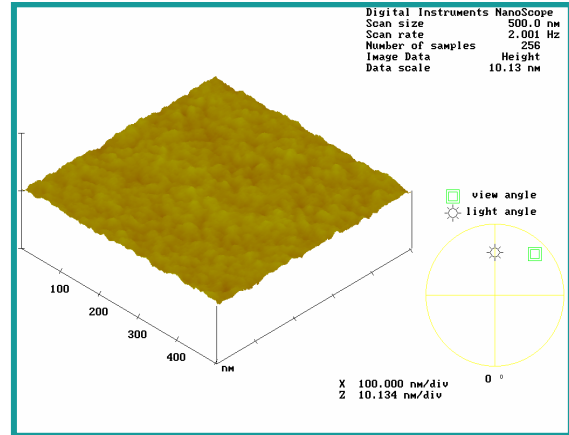


Fig. 3c. AFM of 1:0.25:1, respectively of TEOS:TMSPM:PMMA, with TiO₂ nanoparticles.

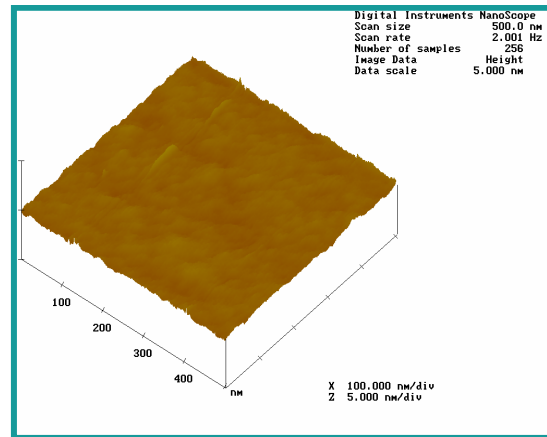


Fig. 3d AFM of 1:0.25:0.5, respectively of TEOS:TMSPM:PMMA, with TiO₂ nanoparticles.

The comparison of the height profiles does not show either nanoparticle agglomeration. These results show that the nanoparticles are very well dispersed in the entire hybrid matrix. The surface hardness of the hybrid coatings was measured by a pencil test according to the ASTM Standard D 3363-92[22]. The application of this test showed that the hardness of all the hybrid coatings is at least 9H. This result shows that the inorganic component in the hybrid coatings has reinforced the organic component producing harder with more abrasion resistance coatings as compared with pure PMMA coating.

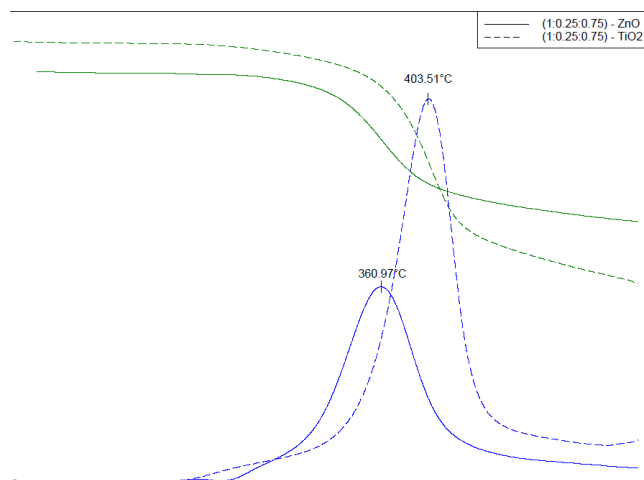


Fig. 4. TGA results.

The TGA results showed (Fig. 4) that the hybrid coatings prepared adding TiO₂ nanoparticles have almost 30°C above to the prepared without nanoparticles to the same composition (1:0.25:0.75) for TEOS: TMSPM:PMMA, this due to the compatibility between the PMMA and TiO₂. Respect to the hybrid coatings prepared with ZnO has almost the same temperature that without nanoparticles, this due to that poor compatibility and no affect the thermal properties of the PMMA significantly, in all the cases shown one principal decomposition step, and the residue corresponds to the another inorganic components.

IV. CONCLUSIONS

In this work, we have applied the sol-gel method to deposit hybrid SiO₂-PMMA-nanoparticles of ZnO/TiO₂ coatings on glass substrates. The results showed that the hybrid coatings are constituted by a homogeneous organic-inorganic matrix with the embedded nanoparticles very well dispersed on it. The surface of the coatings is very smooth and flat with very low roughness and reinforced hardness in comparison with the PMMA phase. The optical quality of the transparent hybrid coatings is very good with transmittance values above 95 % in all the range of visible spectrum. All the hybrid coatings have good thermal stability and for the prepared adding TiO₂ nanoparticles are better than without them.

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