

Chapter 30

Multifunctional Polymer/Nano-TiO₂ Photochromic Hybrid Coatings as a Barrier for Protection against Corrosion

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ABSTRACT

This chapter shows results related to synthesizing hybrid materials composed of polymer matrix/nano-TiO₂, which possesses a photochromic property under UV irradiation. The synthesized TiO₂ was amorphous, but, for the hybrid photochromic response, the required illumination is that with the same or superior energy than semiconductor bandgap. Moreover, the photochromism requires OH proportionate to preparing within an alcohol, and by releasing them by temperature, the color change resulted permanent. The hybrid materials were prepared as coatings, which display multifunctional characteristics. The polymeric matrix was proven with different kinds of organic polymers and solvents. This phenomenon was investigated through Salt Spray Test, Electrochemical Impedance Spectroscopy, HRTEM, SEM, Reflectance, Fluorescence, Contact Angle, and EPR. The capacity to act as a barrier for corrosion protection was investigated. Finally, the hybrid material is proposed as an indicator for applications in engineering.

INTRODUCTION

Chromogenic materials of both organic chemistry-purely based, hybrid of inorganic-organic species, inorganic-doped and semiconductor-type have been widely studied and applied in a variety

of fields, such as: micro-electronics, detectors, domestic uses, medicine, etc. These areas need materials with a capacity of color change under different kinds of stimuli, such as: optical, electrical, thermal, mechanical or chemical.

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These needs of chromogenic materials may lie on transition metal compounds because its optical properties and low cost made them of constant interest in materials research. Hybrid and composites inorganic-organic materials based on polyester polymers and titanium hydroxide species have been prepared by the sol-gel process.

The whole hydrolysis and condensation process results in multiple chromogenic materials. FT-IR, UV-vis, ESR spectroscopic results show the formation of hydrogen bonds between titanium hydroxide and polyester species, $n-\pi^*-\pi-\pi^*$ reversible transitions after light excitation, permanent complex formation after thermal stimulus and ionization of titanium oxide species after polar solvent excitation.

Anticorrosive, antiabrasive, hydrophilic and coloration properties of the hybrid coatings have also been investigated through electrochemical impedance spectroscopy (EIS), Salty spray test (SST), Taber test, Scanning Electron Microscopy (SEM) and contact angle measurements. The results show good anticorrosive properties of hybrid coatings at low titania sol-gel concentrations and high boiling point polymer solvents, highly hydrophilic coatings when combined with aluminum hydroxide sol-gel particles, the high velocity of coloration and low velocity of discoloration at UV and solar light exposition.

BACKGROUND

Photochromic materials, classified as organic or inorganic, have existed since the end of the XIX century. Photochromic materials change their optical properties when they are exposed to visible or UV light and reverse properties in the darkness. Basically, the phenomenon consists of a reversible change of isolated chemical species between two states with different absorption spectra. A widely known inorganic photochromic material is one used in photochromic lenses, which use metallic halides, such as: AgBr or AgCl. When UV light illuminates these glasses, the metallic halide

crystals dissociate into metallic silver and halide. This effect causes absorption in the visible range. When removed from the light source, the metallic halide thermally recombines and recovers its original color and glass transmission. The typical optic response for photochromic glasses in colored and discolored states takes 3-4 minutes at room temperature, with an approximate typical optical response of $T = 85-50\%$. This study presents hybrid materials consisting of titanium oxides obtained by the sol-gel process in a polymeric matrix, the combination of which constitutes a system with color centers that can absorb in a wide range of the visible spectrum, resulting in a brown tonality. Color changes are caused by the energy at which, electron-hole pairs are generated in the system. It is assumed that this propitiates a valence change of titanium oxide/hydroxide in an OH radical environment inside of a surrounding polymeric matrix.

There are many varieties of photochromic materials with quite different physicochemical principles. Organic photochromic materials have excellent color and tonality, but due to the great need to improve their characteristic absorption in the visible spectrum, which can be a basis for effective coloring, the molecular structure must often contain a delocalized π -electron.

Molecules associated with this type of electronic structure, polycyclic aromatic hydrocarbons, pigments, and heterocyclic quinoline azo-dyes, are often carcinogenic, penetrating skin and having a high toxicity risk (Beamson ET AL., 1992). Major problems faced by photochromic compounds include stability loss when repeatedly exposed to intermittent or continuous radiation in the air. This leads to decay in a few days, with a consequent lower response to light (Li-Qiong ET AL., 1994). To address these problems, additives or other polymeric materials are added to increase resistance. These are not always compatible, due to photochromic material-matrix interactions. Their photochromic response can be strongly modified by the presence of polar groups, as these may induce complexation, protonation, stiffness

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