Encapsulation of active compounds for incorporation in multifunctional coatings

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INTRODUCTION AND OBJECTIVES

Currently, most of the objects present in our daily life are coated materials. The activities on development of new coatings with novel features have drastically increased in recent times (Ghosh 2006).

The most common coating applications are for protective, decorative or functional purposes, or a combination of these. "Functional coatings" is a term used to describe surface treatments which possess an extra functionality, with respect to the classic coating properties (Ghosh 2006). The new functionality is normally provided by additives or by matrix functionalization. However, the direct addition of active compounds to polymer can often promote negative effects on the final applications, namely deactivation of the active compound due to its interaction with coating matrix, promoting their degradation and spontaneous leaching (Raps 2009). One way to overcome these problems is the encapsulation of active compounds in 'smart' micro and nanocontainers that release the encapsulated compounds in response to specific stimuli.

The purpose of this work is the encapsulation of active species (namely corrosion inhibitors, indicators and biocides) in two types of capsules (silica and polyurea), and their subsequent incorporation in coating formulations to render new functionalities to the final coating, namely self-sensing and self-healing from a corrosion protection perspective.

MATERIALS AND METHODS

In this work, aluminum alloy 2024 (AA2024) was used as substrate. The active compounds selected for encapsulation was the pH indicator phenolphthalein (PhPh) and the corrosion inhibitor 2-mercaptobenzothiazole (MBT). All the chemicals were analytic grade and were used without further purification.

Two different systems were used for the encapsulation of active compounds (PhPh and MBT), polyurea microcapsules (Pu_MC) and silica nanocapsules (Si_NC), as described in figure 1. Briefly, two solutions were prepared, one based on water, hydrophilic monomers and surfactants and the other with hydrophobic monomers and the active compound to be encapsulated dissolved in organic solvent. Afterwards, these were mixed under constant stirring in order to achieve an oil-in-water emulsion. Polymerization occurs at the interface of the immiscible phases, with the active compounds encapsulated within the formed capsules: polyurea microcapsules and silica nanocapsules.

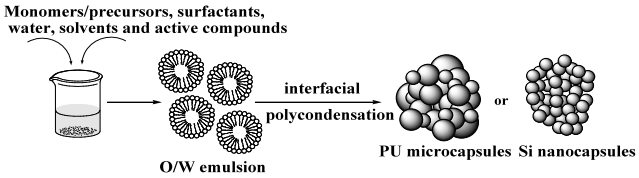

Figure 1: Schematic synthesis of capsules with encapsulation of active compounds.

The synthesized capsules were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG) and nitrogen adsorption-desorption isotherms. The release of active compounds was monitored by high performance liquid chromatography (HPLC) and by UV-Vis spectroscopy.

The produced capsules were incorporated in a water-based model epoxy coating formulation. Then, aluminum alloy 2024 substrates were coated with the modified formulations and cured at room temperature for several hours. For sensing purposes, the coated substrates were immersed in a corrosive electrolyte to display corrosion onset by color change, while for assessment of anticorrosion the coated substrates were immersed in a NaCl solution and characterized by Electrochemical Impedance Spectroscopy (EIS).

RESULTS AND DISCUSSION

Pu_MC and Si_NC were prepared through an oil-in-water microemulsion polymerization. Pu_MC results from the polymerization of a diisocyanate with a diamine, while Si_NC results from the alkaline polymerization of a silane. Both types of capsules with MBT shows a yellow pale color while the capsules with PhPh shows a pink pale color in alkaline conditions.

The synthesized Pu_MC capsules show regular spherical shape with a broad size distribution, between 50 nm and 1 μm in diameter, while Si_NC are spherical and porous, with a narrow size distribution, between 100-150 nm (figure 2). The encapsulation of the active compounds does not promote any significant structural or morphological change in the capsules.

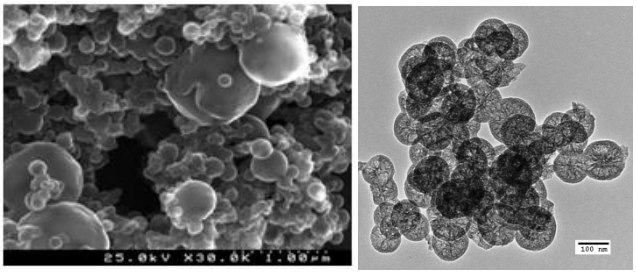

Figure 2: SEM picture of Pu_MC (left) and TEM picture of Si_NC (right).

FTIR tests were performed to confirm the presence of active species (MBT and PhPh) in the developed capsules. TG measurements were performed to verify the thermal stability of both capsules and to determine the amount of MBT and PhPh encapsulated. Si_NC demonstrate good thermal stability and a loading content of 10 wt% for MBT and 9 wt% for PhPh.

Release studies showed that each type of capsules has a release mechanism associated. Si_NC releases the active compound by diffusion through pores, with pH having a significant impact on release extent. On the other hand, Pu_MC releases the active compounds after mechanical breakdown or by thermal stimulus, with temperature increase causing a greater fluidity of the polymer on the walls of polyurea capsules and increase of permeability.

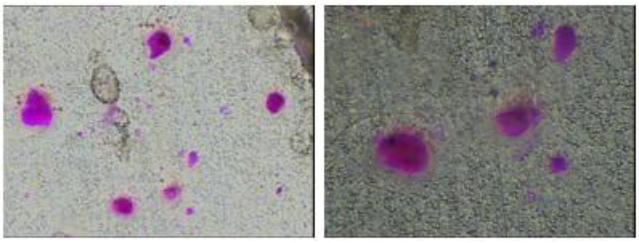

Figure 3: Optical photographs denoting the self-sensing performance of capsules with PhPh associated with the onset of corrosion processes.

AA2024 substrates were coated with a model formulation, doped with Si_NC-PhPh or Pu_MC-PhPh, and subsequently immersed in a corrosive electrolyte (NaCl solution) to reveal the onset of corrosion. The beginning of corrosion promotes a local increase of pH in cathodic regions, and that increase is displayed by the capsules with PhPh due to color change as shown is figure 3. Coatings doped with either Si_NC-PhPh or Pu_MC-PhPh show pH-sensing activity.

Figure 4 shows the evolution of corrosion of AA2024 immersed in 0.05 M NaCl solution in the presence of empty capsules and capsules with MBT. The active corrosion protection results from MBT release and consequent interaction with the metallic substrate (Maia 2012).

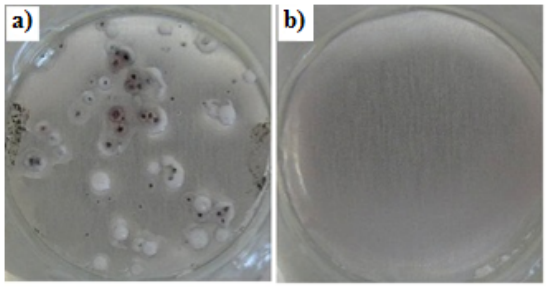

Figure 4: Optical photographs showing the evolution of corrosion on AA2024 immersed in NaCl solution in the presence of a) empty capsules and b) capsules loaded with MBT.

CONCLUSIONS

Two different types of capsules were synthesized and used for the encapsulation of two selected active compounds, namely phenolphthalein and 2-mercapsubenzothiazole. Both types of prepared capsules exhibited a spherical morphology. Polyurea capsules were obtained with a broad size distribution in the micrometer/sub-micrometer range while silica capsules show a narrow size distribution in the nanometer range.

Coating loaded with PhPh capsules shows corrosion-sensing functionality, and capsules loaded with MBT display anticorrosion properties, thereby protecting AA2024 substrate against corrosion.

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