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# Addition of graphene oxide plates in cataphoretic deposited organic coatings

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ABSTRACT

This work aims to verify how the addition of graphene oxide into the cataphoretic bath goes to modify the properties of the obtained coating. Because a simple single-step deposition produced a strange morphology deposit, other combinations consisting of two deposition steps were done, in order to make the coating even more homogeneous and protective. Particular attention is therefore paid to the importance of the intermediate curing process, between the two deposition steps. The morphology of the coatings is analyzed by both optical and scanning electron microscopy, to measure the thickness of the protective layers and their defective properties. Finally, corrosion resistance properties of the coatings are evaluated by salt spray chamber exposure and electrochemical impedance spectroscopy measurements. It appears evident that the graphene oxide leads to the creation of defective layers, with the consequence of decreasing the durability of the coating. However, by depositing in two steps, with two different baths, it is possible to preserve the integrity of the coating, ensuring the protection of the substrate.

## 1. Introduction

Polymer Matrix Composites (PMCs) are a class of materials of great interest in the industrial world, as they are relatively easy to produce and have a high strength-to-weight ratio, a property required for different types of applications. Epoxy resins are the most widely used polymers in the coating industry, thanks to their good mechanical properties, adhesion to substrate, dimensional stability, good chemical resistance and low cost [1,2]. The epoxy resin, however, shows a brittle behavior [3,4] and permeability to aggressive agents [5–7]. Several studies have been carried out to improve the properties of epoxy coatings. For example, the fracture toughness can be improved by the incorporation of metallic oxides [8,9], clays [10–12], carbon nanotubes [13–15] and carbon-based materials [16–18]. A concrete possibility for improving the properties of an epoxy coating is the use of graphene.

Thanks to the experiments concerning graphene by Konstantin Novoselov et al. of the University of Manchester in 2004 [19], graphene has quickly become an important material, subject of many studies. It is composed of a honey-comb structure made of $sp^2$ bonded carbon atoms: this structure gives graphene excellent electrical [20–22], thermal [23–25] and mechanical [26,27] properties, allowing it to be used in various fields, including electronics [28] and aerospace industry [29] and bio-engineering [30].

Particular attention has been paid to the ability of graphene to improve the protection against corrosion of organic coatings through the barrier effect exerted by its sheets [31]. However, these sheets tend to agglomerate, due to strong Van der Waals forces and π π bonds [32,33]. Graphene must therefore be homogeneously dispersed into the polymer matrix in order to fully exploit its protective properties. An effective method for obtaining a good dispersion is the use of graphene oxide (GO), which shows functional carboxy, hydroxyl and epoxy groups on its surface that alter the Van der Waals interactions. Graphene oxide presents a disturbance of its $sp^2$ bonding network, resulting as an electrical insulator. In order to restore its electrical conductivity, GO must be partially reduced, recovering the honeycomb lattice of graphene. Various studies have been concerned with the use of GO to improve the corrosion protection of epoxy coatings [34–40], but studies have not yet been carried out on deposition of epoxy-GO coatings by the cataphoresis.

With the cataphoretic deposition process it is possible to obtain coatings with excellent properties in terms of adhesion and corrosion resistance [41–44]. This technique is often used in the automotive world, because it is easy to use and cost-effective.

In literature there are no papers that deal with the improvement of the electrodeposition process by cataphoresis, in general. Since cataphoresis is a simple technique, but at the same time very effective, we have never focused on the possible approaches to improve the process and the anti-corrosion properties of the coatings that can be obtained. As provided by this deposition process after polymer deposition a curing thermal treatment is necessary to produce the cross-linking of

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the polymeric chains to form the protective coating.

The novelty of this work lies in the use of this deposition technique to create GO-epoxy composite coatings, exploiting the excellent properties of the cataphoresis process, already optimized at an industrial level. This technique could in fact allow to realize composite coatings in a short time, in an economic and automated way.

In this paper cataphoresis has been used to realize an epoxy-GO coating, trying to identify the process parameters that provide better guarantees in terms of protection of the substrate. Thanks to its particular properties, graphene oxide, if properly reduced, could be exploited in order to obtain conductive 'smart' coatings. It should therefore be verified that the GO addition into a cataphoretic bath does not cause problems during the deposition process, and therefore makes the coating ineffective.

To obtain these epoxy-GO coatings, an aqueous solution of graphene oxide is added into a typical industrial epoxy-based cataphoretic bath. In addition to the use of two values of applied voltage, different treatment combinations are also studied, using two-step depositions, with and without baths containing GO. The influence of the applied voltage value on the properties of the coating obtained is evaluated for each type of combination performed. The use of two different baths, for the same duration of treatment, allows the obtaining of coatings of different thicknesses and with complex surface morphology. The short thermal cross-linking process (only 5 min instead of 20 min recommended by the supplier) between the two deposition steps also involves considerable differences in the coatings obtained in terms of homogeneity and protective properties of the coatings themselves. These coatings have been therefore observed by optical and electronic microscope to analyze their defectiveness and thickness dimensions. The behavior of the samples in aggressive environment has been then evaluated by accelerated corrosion testing and impedance measurements, in order to verify the goodness of the coating treatment.

## 2. Experiments

45 mm x 70 mm mild carbon steel samples (Q-panel type R supplied by Q-lab, Westlake, OH, USA) were used as substrate. In order to increase the adhesion between cataphoretic coating and steel substrate, the samples have been pre-treated, using a 2 min degreasing in acetone, with the application of ultrasound stirring, followed by sandblasting process. A mechanical surface pretreatment, using corundum powder (0.2 mm diameter – 70 mesh) has been chosen because it is a simple and fast process and ensures excellent adhesion to the coating layer. A second acetone cleaning of two minutes stirring was carried out, then, to remove the possible presence of abrasive powders on samples' surface.

An epoxy-based bath (ARSONKOTE 212 2 K CATA TIN FREE EPOSSIDICA BLU X35-A17 supplied by Arsonsisi, Lainate, Mi, Italy) has been chosen as the epoxy resin ensures excellent adhesion level and good mechanical properties of the coating [45]. In addition, the graphene oxide being rich in epoxy groups on its surface, its dispersion into an epoxy matrix is facilitated. The standard deposition bath (40 wt% resin – 60 wt% distilled water), called 'Blue', shows a pH value of 5.6. A 300 mm x 50 mm stainless steel plate was used as anode, placing it in the bath at a distance of 80 mm from the sample.

A second bath was then made, called 'Black', adding the solution of GO (Graphene Oxide Water Dispersion - 0.4 wt% concentration), supplied by Graphenea, Donostia, Gipuzkoa, Spain) instead of simply distilled water into the formulation of the Blue bath. The Black bath (40 wt % resin – 60 wt% GO solution) contains a final 0.24 wt% concentration of GO and shows a pH value of about 5.3. This decrease in pH, compared to the Blue bath, is given by the acidic pH of the Graphenea solution, equal to 1.8. The deposition setup (type of anode and cathode-anode distance) has been the same as for the Blue bath.

It has been chosen to evaluate the influence of two different values of voltage applied, the most important process parameter in a cataphoretic deposition process, while the deposition time has been maintained constant at 120 s, as recommended by the cataphoretic bath supplier. The different samples have been coated applying 200 and 250 V. The 250 V is the maximum limit that can be used for depositions, as higher voltages have led to a strong bubble development for hydrogen evolution, especially in the Black bath. This does not mean that the evolution of hydrogen can be underestimated below 300 V of application: the entrapment of bubbles inside the coating can reduce its protective properties, and represents a defect that must be kept under control. No voltage values higher than 250 V were applied to prevent the development of eddy currents and consequently the development of hydrogen. Under 200 V instead, it was difficult to obtain coatings of thickness greater than 10 microns, so the 200 V were taken as the lower limit.

The Blue bath was used to make a comparison with Black bath coatings, verifying whether or not the addition of graphene oxide in the bath resulted in a real improvement in corrosion protection for the substrate.

Since it was immediately observed that the morphology of coatings obtained with Black bath deposition is very complex, non-homogeneous and probably non-protective, it was decided to make 2-step depositions using both baths.

In order to realize coatings with more homogeneous thickness, it was decided to use the Blue bath for a short deposition of 5 s, followed by the actual deposition with the bath containing GO for another 115 s, for a total duration of 120 s. It was then chosen to verify which influence could have the curing of the first layer obtained with Blue bath, so samples were coated with and without curing of 5 min, at 160 °C, between one step and the other of deposition.

Finally, it was decided to reverse the order of the 2 baths, depositing first with Black bath and then with the Blue one, to see which combination could give the best guarantees from the point of view of the substrate corrosion protection.

At the end of the deposition, all the samples were subjected to curing at 160 °C for 20 min as recommended by the supplier.

In Table 1, all the different deposition combinations are schematized, with the nomenclature chosen for the samples.

The coated samples have been observed by the optical stereomicroscope (Nikon SMZ25) and environmental scanning electron microscope (ESEM JEOL IT 300) in order to observe the particular morphologies obtained. The coating thickness was measured with the Phynix Surfix digital thickness gauge.

The behavior of the coated samples in an aggressive environment has been tested by exposure in a salt spray chamber for 500 h, following

**Table 1**
Nomenclature of the samples, with different deposition combinations.

| Sample | Voltage V | Step 1 | Curing 1 (160 °C) | Step 2 | Curing 2 (160 °C) |
|---|---|---|---|---|---|
| A1 | 250 V | 120 s Blue | – | – | 20 min |
| A2 | 200 V | 120 s Blue | – | – | 20 min |
| B1 | 250 V | 120 s Black | – | – | 20 min |
| B2 | 200 V | 120 s Black | – | – | 20 min |
| C1 | 250 V | 5 s Blue | – | 115 s Black | 20 min |
| C2 | 250 V | 5 s Blue | 5 min | 115 s Black | 20 min |
| C3 | 200 V | 5 s Blue | – | 115 s Black | 20 min |
| C4 | 200 V | 5 s Blue | 5 min | 115 s Black | 20 min |
| D1 | 250 V | 5 s Black | – | 115 s Blue | 20 min |
| D2 | 250 V | 5 s Black | 5 min | 115 s Blue | 20 min |
| D3 | 200 V | 5 s Black | – | 115 s Blue | 20 min |
| D4 | 200 V | 5 s Black | 5 min | 115 s Blue | 20 min |