

# Deposition of hybrid sol-gel films on hot dip galvanized reinforcing steel

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## Summary

A functionalized siloxane and five amino terminated oligopolymers were used to produce, by sol-gel method and using a dip-coating process, organic-inorganic hybrid (OIH) coating films as an alternative pre-treatment to prevent the corrosion of galvanized steel in concrete. The influence of residence time ( $R_T$ ), cure and number of dip steps on the coverage and uniformity of the obtained coatings dipped at a withdrawal speed of  $10 \text{ mm min}^{-1}$  for each oligopolymer were studied. The surface morphology and the depth chemical composition of the obtained coatings were analysed by SEM/EDS and GD-OES techniques, respectively. The results showed that the coverage and uniformity of the OIH coating deposited on the HDGS surface improves with the increase on  $R_T$  and number of dip steps. Nevertheless, full coverage is seldom achieved and the final OIH coatings thickness is very irregular.

## 1 Introduction

The use of hot dip galvanized steel (HDGS) has been recognized as one effective measure to increase the service life of reinforced concrete structures in marine environment<sup>1</sup>. In the early stages of contact between zinc and alkaline media ( $\text{pH} > 12.8$ ), hydrogen evolution may occur<sup>1-3</sup>. This reaction involves a high consume of zinc during the passivation process and induces a delay in developing the forces of adherence between reinforcement and concrete. To mitigate the consequences of the hydrogen evolution process, chromate conversion layers have been used. However, Cr(VI) compounds are carcinogenic and toxic and due to environmental requirements are forbidden. Some organic-inorganic hybrid sol-gel coatings (OIH) have been proposed as alternatives<sup>4-7</sup>. Despite the promising physical and chemical characteristics of the OIH coatings the formed gel coating obtained from a precursor liquid mixture and the characteristics of the obtained coating are dependent of processing conditions. However, the barrier effect and the performance of an OIH sol-gel film as a pre-treatment to reduce the formation of excessive amounts of zinc oxides, as well the  $\text{H}_2$  evolution, besides processing conditions, is also highly dependent on the coating deposition method.

In this work factors such as residence time ( $R_T$ ), cure between each deposition by dipping technique and the presence of one, two and three layers were studied in order to enhance the barrier properties of OIH coatings as well to get a coating with an uniform distribution.

## 2. Experimental Procedure

### 2.1. Reagents

The OIH gel matrices were prepared following a well-established methodology described elsewhere<sup>8,9</sup>. Five different structural types of ureasilicate organic-inorganic hybrid (OIH) gel matrices were prepared by a reaction between the isocyanate group of the derived siloxane (ICPTES) with five different di-amino functionalized polyether

with different molecular weights (Jeffamine D-230 ®, Jeffamine D-400 ®, Jeffamine ED-600 ®, Jeffamine ED-900 ® and Jeffamine ED-2000 ®).

All the used Jeffamines and the functionalized siloxane, 3-isocyanate propyltriethoxysilane (ICPTES), were used as supplied. Ethanol (absolute 98 %, Riedel-de-Haën), citric acid monohydrate (Merck), were also used as received. Ultra-pure water (0.055-0.060  $\mu\text{S}/\text{cm}$ ) obtained from a Purelab Ultra System (Elga) was used.

## **2.2. Coating deposition**

Coatings were applied over HDGS metal 5.0x1.0x0.1 cm plates cut from commercially available sheets. The curing of the coated HDGS samples were performed in an incubator-compressor (ICP-400, Memmert) and kept at 40°C for about 15 days. HDGS coating samples were prepared by dipping HDGS metal plates on prepared mixtures at a withdrawal speed of 10 mm min<sup>-1</sup> without residence time ( $R_T = 0$ ) and with a residence time of 100s ( $R_T = 100\text{s}$ ) using a dip coater (Nima, model DC Small). Coated samples were prepared with one, two and three dipping steps using always the same conditions for curing (15 days at 40°C between each dipping step). OIH coatings prepared were identified as U(X) where X represents Jeffamine molecular weight.

## **2.3 Glow Discharge Optical Emission Spectroscopy (GD-OES)**

The depth profiling chemical composition of coatings applied on HDGS were performed using a glow discharge optical emission spectrometer on coated and uncoated substrates. A LECO glow discharge GD OES 850A, with a radiofrequency source and a 700 V RMS was used and samples were analyzed under argon atmosphere.

## **2.4 Scanning electron microscopy (SEM/EDS)**

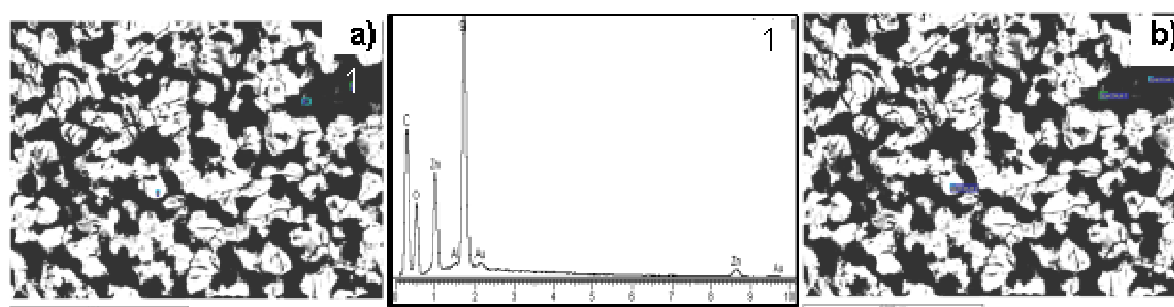
OIH sol-gel coatings applied on HDGS specimens were studied with a scanning electron microscope (SEM, JEOL JSM-6400) coupled with a EDS detector (Inca-xSight Oxford Instruments). The surface of specimens was covered with an ultrathin coating of gold deposited by sputter coating.

# **3. Results and Discussion**

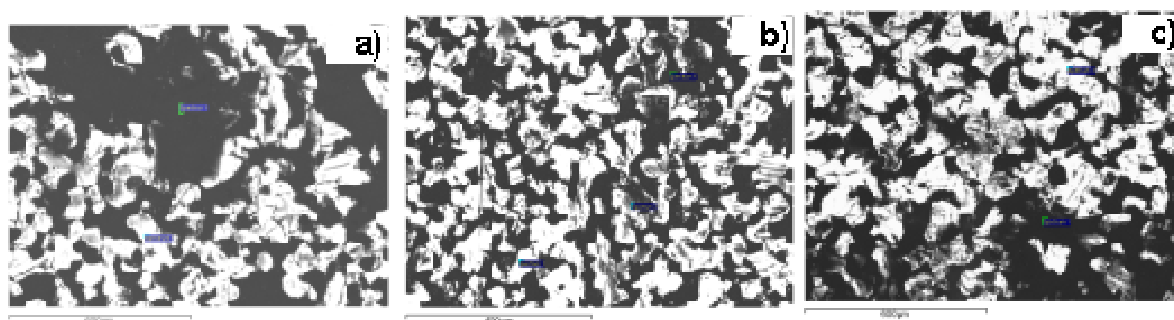
The thickness of the OIH coatings prepared was determined by GD-OES from the presence of Si on the surface of the sample. Representative results are presented in Figure 5. For every conditions studied, Si was detected in a range of 21 to 37  $\mu\text{m}$  of coating depth and OIH coating thickness increased with Jeffamine molecular weight,  $R_T$  and number of dipping steps.

SEM/EDS studies show that, for all OIH synthesized the coating covers the HDGS substrate regardless of the number of dips, with cures between each dip step with or without  $R_T$ . Representative SEM images and EDS analysis data, obtained for different HDGS samples coated with OIH U(230), OIH U(400), OIH U(600) and OIH U(900) are presented in Figures 1 to 4. The lighter areas match with the presence of Zn and the darker areas match with the presence of OIH, justified by EDS analysis as these reveal high intensity peaks of C, Si and O. It is clear that all the OIH coating covered the HDGS surface even when  $R_T = 0\text{s}$  and only one dip step was applied. Figures 1a) and 1c) show that when one layer is deposited over the HDGS the coating distribution and the uniformity does not improve with the increasing of  $R_T$ . However, substantial improvements occur when the  $R_T=100$  and three layers are deposited with cures between each dip step Figures 3a) and 4a). Nevertheless, a full coverage is not achieved and a compromise must be found between the time and energy consuming and the performance/barrier properties of the OIH coating. From Figure 4

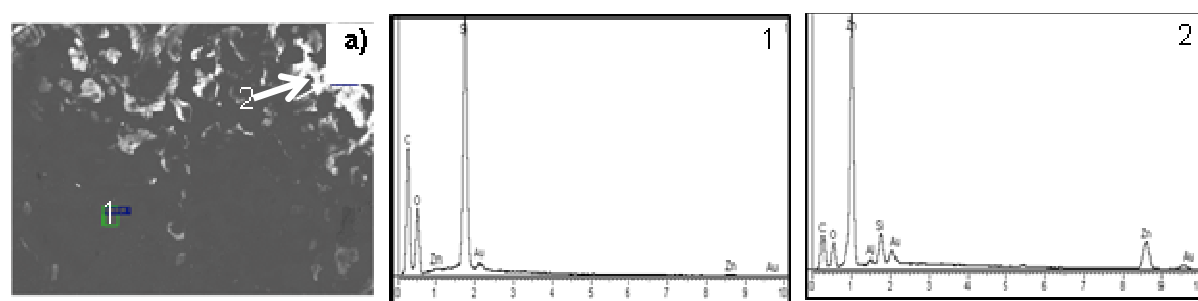
it can be observed that as the molecular weight of the di-amino functionalized poly-ether is changed to higher values, from Jeffamine D-400 ® (Figure 4a)), to Jeffamine ED-600 ® (Figure 4b)) and to Jeffamine ED-900 (Figure 4c)) a more uniform coating is obtained under the same conditions.



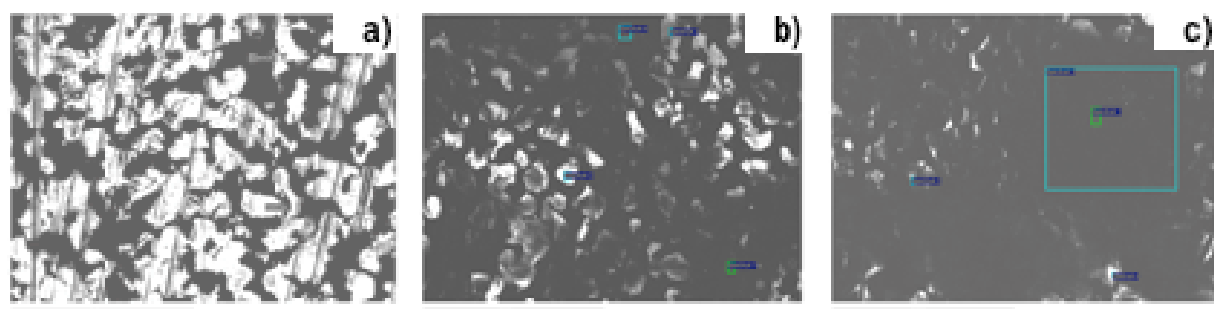
**Figure 1.** a) SEM image of sample U(230) ( $R_T=0s$ ; one dip step) with the localization of EDS analysis 1 and b) SEM image of sample U(230) ( $R_T=100s$ ; one dip step).



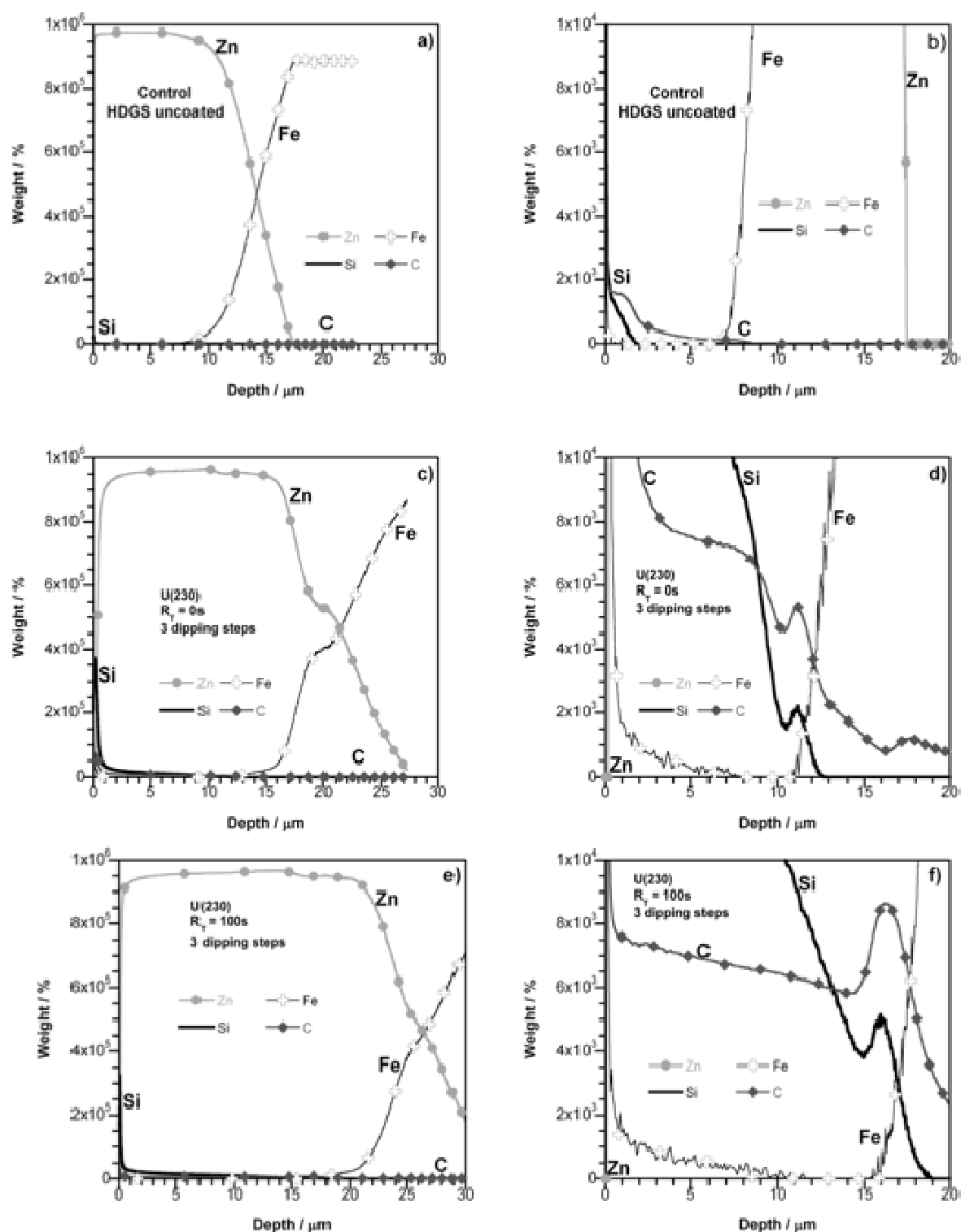
**Figure 2.** SEM images of samples: a) U(230) ( $R_T=0s$ ; three dip steps), b) U(400) ( $R_T=0s$ ; one dip step) and c) U(400) ( $R_T=0s$ ; two dip steps).



**Figure 3.** a) SEM image with the localization of EDS analysis 1 and 2 of sample U(230) ( $R_T=100s$ ; three dip steps).



**Figure 4.** SEM images of samples: a) U(400) ( $R_T=100s$ ; one dip step), b) U(600) ( $R_T=100s$ ; one dip step) and c) U(900) ( $R_T=100s$ ; one dip step).



**Figure 5.** a) GD-OES depth profiles for Zn, C, Fe, Si within HDGS substrates for a) control, c) U(230) ( $R_T=0\text{s}$ ; 3 dip steps) and e) U(230) ( $R_T=100\text{s}$ ; 3 dip steps). b), d) and f) shows a detailed view of recorded profile, for the same elements, from plots a), c) and e), respectively.

## 4 Conclusions

It was concluded that the coverage and uniformity of the OIH coating deposited on the HDGS surface improves with the increase on residence time ( $R_T$ ) and number of dip steps. However, due to the high roughness of substrate, full coverage is seldom achieved and the final OIH coatings thickness is very irregular even with cures between each deposition. It was also verified that, changing  $R_T$  from 0s to 100s, increases, under the same conditions, the thickness of the OIH coating. Electrochemical studies should be performed in order to evaluate the influence of the coating preparation on the corrosion behavior of the OIH pretreated galvanized steel.

## 5 References

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