

DEVELOPMENT OF NON-TOXIC POLYMER COATINGS WITH IMPROVED BIOFOUL RELEASE PROPERTIES

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Introduction

On a ship's hull biofouling, which is the attachment of marine organisms on marine vessels and structures, leads to an increase in the hydrodynamic drag and therefore to increased power requirements and/or reduced speed. Presently used ablative coatings that contain biocides such as cupric oxide or organo-tin compounds are non-selective and have a negative environmental impact.

The aim of this project is to develop non-toxic, environmentally friendly polymer coatings that minimize biofouling and protect steel from corrosion. Since siloxanes and fluorosiloxanes have been shown to be effective non-toxic foul release materials, siloxanes that contain pendant perfluoroalkyl groups have been prepared and the properties of their UV cured films with photo-acid catalyst have been studied using various techniques including EIS [1]. Similar fluorinated siloxanes have also been converted to solid films by thermal cure with α,ω -diaminoalkanes [2].

Experimental Approach

Two fluorinated pentasiloxanes (A, where $R_f = CH_2CH_2CF_3$ and B, where $R_f = CH_2CH_2(CF_2)_3CF_3$) and a nonfluorinated pentasiloxane (C, where $R = CH_3$) have been prepared as previously reported [1, 2]. Depending on terminal epoxy group type, two different crosslinking/cure chemistries were utilized. The first type of crosslinking reaction involved room temperature UV cure with a photo-acid catalyst ("A", "B", "C") [1]. The second crosslinking reaction was the phenol-catalyzed thermal crosslinking of A or C with α,ω -diaminoalkanes [$NH_2-(CH_2)_n-NH_2$, where $n = 6$ ("A6" or "C6"), 8 ("A8" or "C8"), or 12 ("A12" or "C12")] [2].

Steel coupons for corrosion testing were prepared as follows. A liquid epoxy-amine primer (3M™ Scotch-Weld EC-1945 B/A) was cast uniformly with a drawdown bar at 0.05 mm onto solvent cleaned steel coupons (low-carbon, cold-rolled steel 0.8 x 76 x 127 mm). The primer was allowed to dry 24h at room temperature and the sample was then placed in a 100 °C oven for one h. The various liquid solutions were each coated over the primer layer at 0.13 mm with a drawdown bar. Liquid layers of each A, B, and C and a photo-acid catalyst (0.5 wt%) were UV-cured for 5 minutes. Liquid layers of each A6, A8, A12, C6, C8, and C12 and phenol catalyst (4 wt%) were cured overnight at 100°C.

Impedance spectra were obtained at the corrosion potential E_{corr} as a function of exposure time to 0.5 N NaCl. The spectra were analyzed using the COATFIT module of the ANALEIS software [3] or the open boundary finite length diffusion (OFLD) model [4].

Experimental Results and Discussion

Fig. 1 shows impedance spectra for mild steel with three different coatings after exposure for 35 days. The frequency dependence of the phase angle at the lowest frequencies indicates that the spectra agree with the OFLD model that describes processes in which diffusion occurs in a porous layer [4]. On the other hand, the spectra shown in Fig. 2 for coatings C6, C8 and C12 agree with the coating model that describes the properties of the polymer coating layer and the corrosion reactions occurring at delaminated areas [3]. Based on the approach described elsewhere [5], the specific resistance ρ of the coating and the delamination ratio $D = A_d/A$, where A_d is the delaminated area and A the total exposed area, have been determined (Fig. 3). The observed values of ρ of about 1 Mohm.cm are typical for polymer coatings and suggest that the coating layer is more or less pore-free. The observed D -values in the range of 0.01 – 0.03 % are quite low. These results and the fact that the impedance spectra did not change significantly with time over a two-week period suggest that the polymer coatings developed in this project provide significant corrosion protection to mild steel exposed to 0.5 N NaCl.

References

1. M. A. Grunlan, N. S. Lee, G. Cai, T. Gaedda, J. M. Mabry, F. Mansfeld, E. Kus, D. E. Wendt, G. L. Kowalke, J. A. Finlay, J. A. Callow, M. E. Callow and W. P. Weber, "Synthesis of $\square\square$ -Bis Epoxy Oligo (1H, 1H, 2H, 2H-Perfluoroalkyl Siloxane)s and Properties of their Photo-Acid Crosslinked Films", Chem. Mater. (in press).

- M.A. Grunlan, N.S. Lee, and W.P. Weber, J. Appl. Poly. Sci. (in press).
- F. Mansfeld, H. Shih, H. Greene and C. H. Tsai, ASTM STP 1188, 37 (1993).
- F. Mansfeld, L. T. Han, C. C. Lee and G. Zhang, Electrochim. Acta 43, 2933 (1998).
- F. Mansfeld and T. S. Tsai, Corrosion 47, 958 (1991).

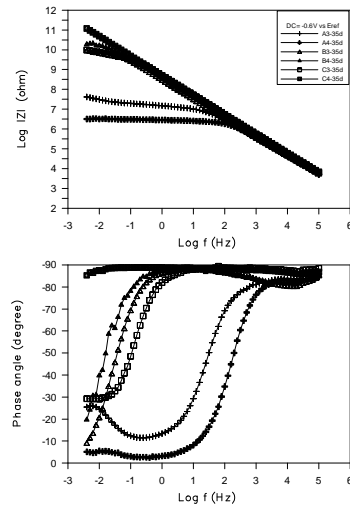


Figure 1. Impedance spectra for mild steel with three different coatings (A, B, C) after exposure for 35 days.

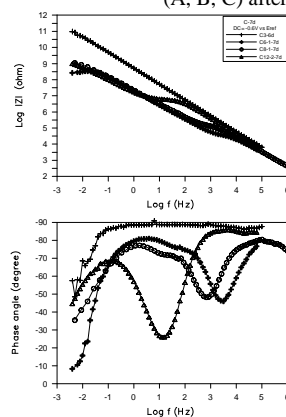


Figure 2. Impedance spectra for coatings C6, C8 and C12 after exposure for 7 days.

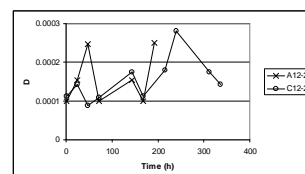
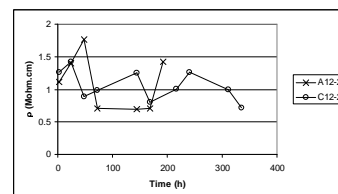


Figure 3. Time dependence of specific resistance ρ of the coating and the delamination ratio D .