Simulation and Development of Tin-Free Antifouling Self-Polishing Coatings

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Summary: TriButylTin based self-polishing coatings (TBT-SPC) were smart solutions to the marine fouling problem. Mechanism of self-polishing were extensively studied and modelled. The aim of this study is to describe the modeling in details and use simulation results to provide insight into the interaction of temprature and some design parameters and a possible basis for accelerated evaluation of new self-polishing coatings.

Keywords: antifouling coating; modelling; polishing rate; TBT-SPC

Introduction

Marine biofouling is a well known problem for ships and boats as the undesirable accumulation of microorganisms, plants, and animals on artificial surfaces immersed in seawater.[1,2] Biofouling increases the hydrodynamic drag, and fuel consumption, it also lowers the manoeuvrability of the sea going vessels.[2]

For nearly quarter of a century, TriButylTin-based Self-Polishing Copolymer (TBT-SPC) antifouling paints provided an efficient and economic means for ship hull protection. However; due to the concerns over the environmental effects of Tin, the use of these coatings is banned worldwide.[3] This has created a major challenge for the scientific and industrial community to formulate replacement systems that meet the performance standards of TBT self-polishing coatings and comply with environmental regulations.[1,4] Since then many short and medium term solutions have emerged based on self-polishing mechanism but with different formulations.

The purpose of this paper is to present the mathematical model that describes SPF mechanism in fair details, then show how it can be used to understand the interactions of parameters and finally develop an accelerated test for evaluation of SPF long term performance.

Working Mechanism of Self-Polishing AF Paints

Figure 1 shows the key phenomena describing behaviour of TBT-SPC coatings. The binder copolymer is tributyltin methacrylate (TBTM) and methyl methacrylate (MMA) which undergoes hydrolysis in seawater. The pigment phase usually consists of seawater-soluble pigments such as Cu_2O [2]. Seawater slowly erodes the binder copolymer through hydrolysis, releasing the TBT-groups as TBTCl (Eq. 1).

$$\underset{TBT-Polymer\ (insoluble)}{Polymer - COO - TBT(s)} + Na^+ + Cl^- \leftrightarrow \underset{Acidpolymer\ (soluble)}{Polymer - COO^-Na^+} + TBTCl(aq) \quad (1)$$

Partially reacted outer layer of the polymer film containing hydrophilic free carboxylate groups becomes weak and easily washed away by moving seawater,

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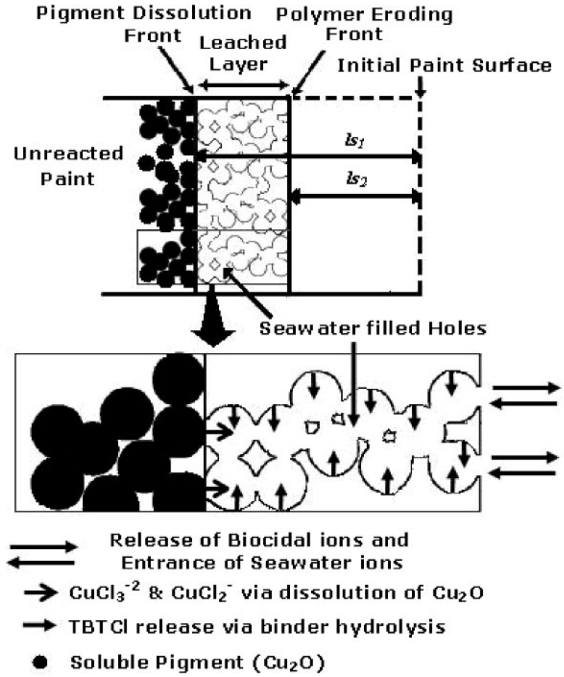

Figure 1.
Schematic presentation of physical phenomena that arises when a TBT-SPC paint is subjected to seawater [5].

(exposing a fresh layer of organotin acrylate polymer (the self-polishing effect).

$$Polymer - COO^{-}Na^{+}(s) \rightarrow Polymer - COO^{-}Na^{+}(aq) \quad (2)$$

Seawater further diffuses into the porous polymer matrix, and dissolves the Cu_2O particles (Eq. 3, 4), resulting in the formation of a leached (i.e. Cu_2O depleted) layer. The dissolved copper forms complexes with Cl_2 ($CuCl_2^-$ or $CuCl_3^{-2}$) that diffuses out of the coating at the surface.

$$1/2\ Cu_2O(s) + H^+ + 2Cl^- \leftrightarrow CuCl_2^- + 1/2\, H_2O(l) \quad (3)$$

$$CuCl_2^- + Cl^- \leftrightarrow CuCl_3^{2-} \quad (4)$$

Our study focuses on finding the concentration of active ingredients, TBTCl and Cu containing compounds ($CuCl_3^{2-}$, $CuCl_2^-$), on the surface of the coating. These active compounds kill or repel the marine organisms as they approach to the surface of the coating and protect the surface from biofouling.[6] In the next section, mathematical model is presented and verified.

Mathematical Modeling

The mathematical model is based on the following rate-influencing steps:

1) dissolution of pigment particles (Cu_2O)
2) hydrolysis and erosion of the active polymer binder
3) effective diffusion in the leached layer
4) external mass transport of relevant species.

The model is based on a single adjustable parameter, X_{max}, which represents the value of surface conversion at which the TBT-polymer is released into seawater.[2] A mass balance over the dissolving pigment front provides an equation for the rate of movement of the front:[2]

$$\frac{dl_{s1}}{dt} = \frac{M_{Cu_2O}\left(D_{e,CuCl_2^-}\nabla_l[CuCl_2^-]|_{l=l_{s1}} + D_{e,CuCl_3^{2-}}\nabla_l[CuCl_3^{2-}]|_{l=l_{s1}}\right)}{2(1-\varepsilon_0)V_{Cu_2O}\rho_{Cu_2O}(1-V_I)} \quad (5)$$

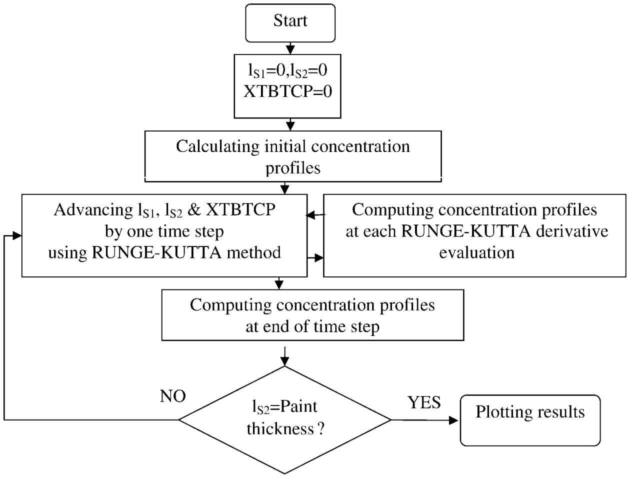

Figure 2.
Solving algotithm.

In this equation V_{Cu_2O}, M_{Cu_2O} and ρ_{Cu_2O} are volume fraction, molecular weight and density of Cu_2O, respectively. $D_{e,i}$ is the effective diffusivity of component i in the leached layer. V_I is the volume fraction of impurities and ε_0 is the initial porosity of paint. Considering a constant value for conversion of active polymer in polymer eroding front, will result in the following equation:

$$X_{TBTCP}\big|_{l_{s2}} = X_{\max} \qquad (6)$$

The boundrary conditions are:

$$l_{s1}(t=0)\ \&\ l_{s2}(t=0) = 0 \qquad (7)$$

Mass balance gives the local conversion of TBTCP (TBTM/MMA copolymer) in the leached layer:[2]

$$\frac{\partial X_{TBTCP}}{\partial t} = \frac{M_{unit} S_0 f_R}{(1-\varepsilon_0)\rho_{TBTCP} V_{TBTCP}}((-r_{TBTCP}) - (-r_{TBTCl})) \qquad (8)$$

In this equation, M_{unit} is the molecular weight of repeating unit of TBTCP. $(-r_{TBTCP})$ and $(-r_{TBTCl})$ are the rate of forward and backward reaction of Eq. 1.

Concentration profiles are calculated using mass balance and equilibrium equations for seawater ions.[2] In this study, finite difference method was used to solve the equations with following algorithm.

Figure 3 shows a good agreement between experimental and simulation results from this study and the one that was reported by Kiil *et al.*[2] for a typical paint named P2.

Parametric Study

There are two types of parameters affecting the performance of coatings:

1) Those related to the paint composition such as pigment particle size, shape, volume concentration, rate of dissolution, retarder volume concentration, rate of binder hydrolysis.
2) Those related to seawater conditions like pH, temperature, salinity and sailing speed.

Effect of these parameters on leaching and polishing rate and TBTCl concentration at the surface of coating, which is essential for the development of Tin free SPC coatings, has been extensively discussed in our previous paper.[5] This paper focuses on the study of parameters interactions that further helps in proper

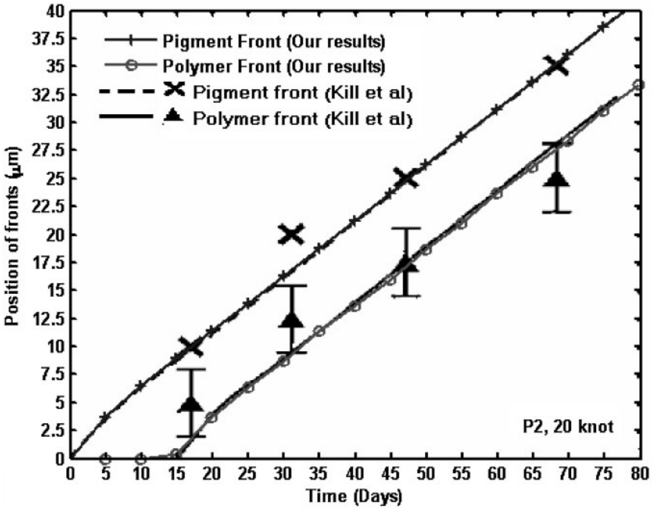

Figure 3.
Comparison between results of this study, Kiil and experimental data at 25 °C. Lines present the results of modeling and symbols show experimental data.

development of Tin free SPC coatings. Specifically, interaction of temperature with other parameters is studied to help in developing accelerated tests.

Interaction of Temperature and Pigment Dissolution Rate

Dissolution rate of the pigment is one of the most important parameters controlling the performance of antifouling paints. The paint performance changes by choosing different soluble pigments with different dissolution rates.[2]

In order to study temperature-dissolution rate interaction two sets of graphs are provided (Figure 4). In the first set, varaition of polishing rate and leached layer thickness as a function of temperature is given at three levels of dissolution rate showing a similar trend. In the next set, variation of the polishing rate and leached layer thickness is shown as a function of dissolution rate at three temperatures indicating that higher polishing rate is expected at higher temperatures. Therefore higher temperature can be used to evaluate the effect of differnt pigment dissolution rate on the polishing rate of the coating.

Interaction of Temperature and Tortusity Factor

The shape of pigment particles is also effective in the behavior of antifouling paints. Pigments with different shapes produce leached layers with different tortusity factors. Tortusity factor is given by the ratio of constriction factor and tortusity[7] and infuence the effective diffusion of ions in leached layer.[2] Higher tortusity factor decreases the rate of diffusion of ions in the leached layer reducing the rate of dissolution and hydrolysis. Higher tortusity factor reduces the thickness of leached layer and polishing rate.[2,5]

Figure 5 shows the varaition of polishing rate and leached layer thickness as a function of temperature at three tortusity levels and variation of them as a function of tortusity at three temperatures. It can be seen easily that leached layer thickness and polishing rate as a function of temprature are showing similar trend in different

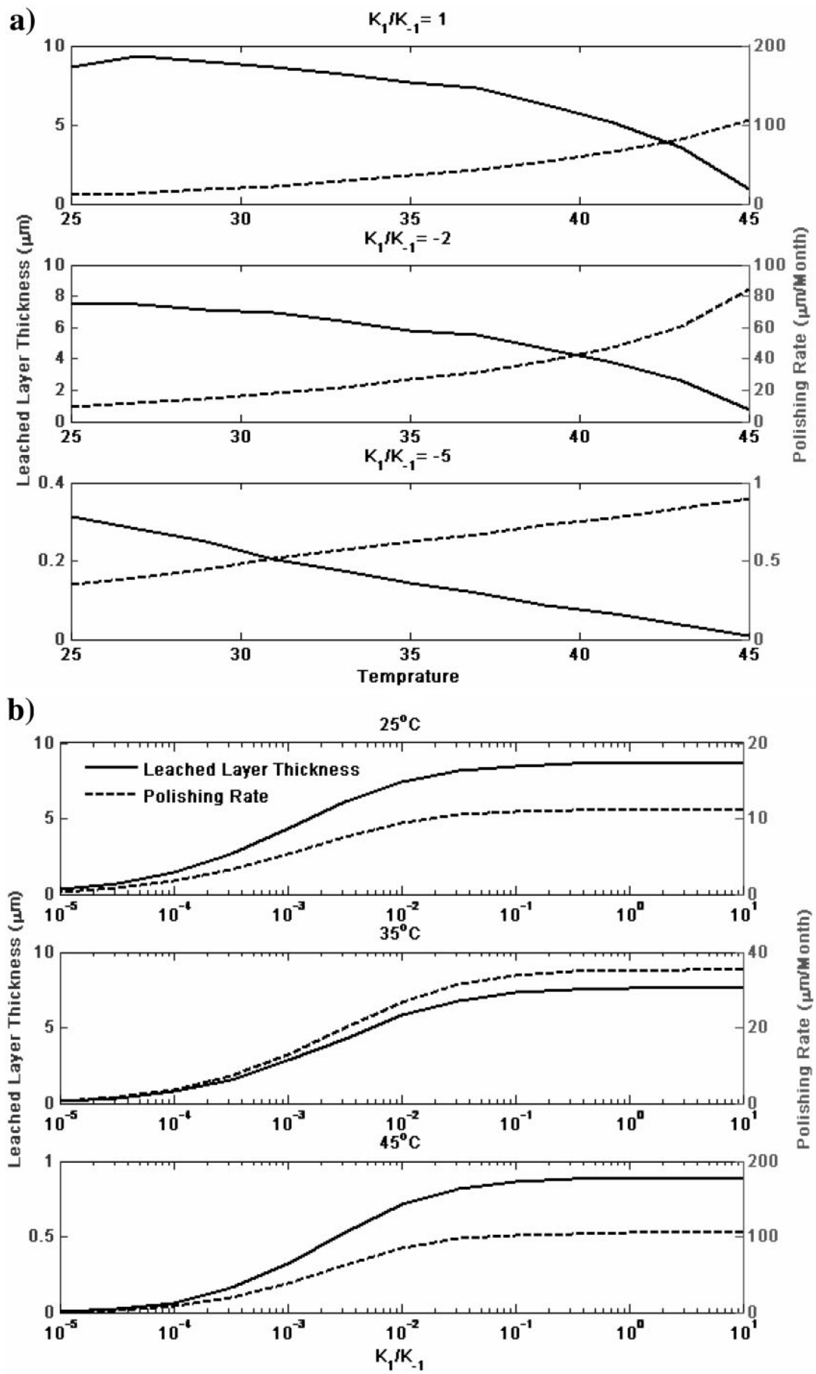

Figure 4.
Variation of polishing rate and leached layer thickness a) At constant dissolution rate b) At constant temperature.

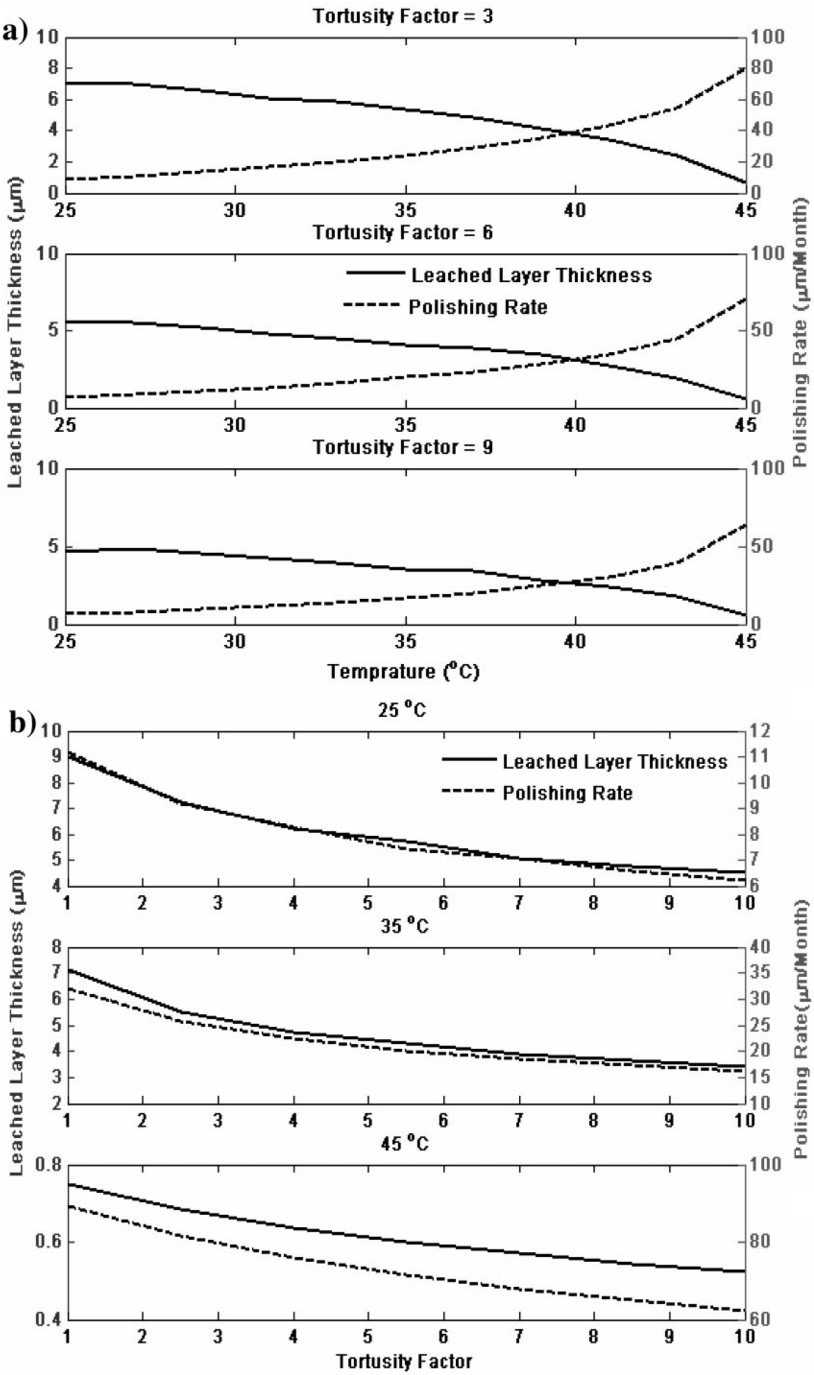

Figure 5.
Variation of polishing rate and leached layer thickness a) At constant tortusity factor b) At constant temperature.

tortusity factors. Figure 5.b shows that higher polishing rate is expected at higher temperatures. Therefore higher temperature can also be used to evaluate the effect of differnt tortusity factors on the polishing rate of the coating.

It must be noted that not all of the parameters follow the same trend, however this study shows that at least two formulation parameters can be studied using temperature accelerated testing.

Conclusion

Mechanism of self-polishing coating has been studied and modeled and now can be used to further development of new tin free formulations. This study takes advantage of the simulation to show that effect of at least two formulation parameters on the long-term performance of SPC coatings can be studied in higher temperature. The higher temperature test accelerates the evaluation and hence the development of new coating formulations.

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