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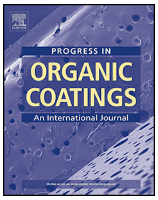

Estimation of organic biocide leaching rate using a modified cavity jump diffusion model

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ABSTRACT

Estimation of biocide lifetime in marine antifouling coatings is of great use to improve and develop technologies. An existing model simulating the diffusion of molecules in polymer networks below glass transition temperature was employed to estimate leaching. This model was modified to allow for swelling due to water uptake and to permit evaluation of copolymer binders as well as homopolymers. This enabled prediction of biocide diffusion coefficients in polymeric coatings of various binder types, including pMMA, a pMMA/butylacrylate binder containing rosin, and a trityl copolymer, using usnic acid as a 'model' biocide. For comparison with modelling results, coatings fomulated using each binder type were also submitted to static and dynamic seawater immersion. Fluorescence microscopy techniques were used to quantify biocide leaching from these coatings relative to unimmersed coatings. Agreement of the modified diffusion model with experimental data was good for pMMA, reasonable for the rosin-based binder, and poor for the trityl binder. Comparison of predicted and experimental biocide profiles in the binder demonstrated deviation from the expected Fickian mechanism for the pMMA binder, despite the accurate rate prediction. This work demonstrates a first approach to predicting organic biocide diffusion, and highlights the areas for future attention.

1. Introduction

The development of antifouling paint coatings to deter the attachment of marine organisms to ships' hulls is of great economic interest. Coatings containing one or more biocidal agents continue to represent a majority of products available on the market. Often, large factorial design experiments must be carried out to assess a vast quantity of formulations and biocide loadings, owing to the complexity of the medium and difficulty in prediction of coating lifetimes. An understanding of the interaction of antifouling biocides within the binder matrix is crucial in predicting their capacity for leaching. The majority of work has focused on the delivery of large pigment biocides such as copper (I) oxide, which rely on reaction with the seawater at the interface in the paint film [1–5], owing to the common use of these in paint mixtures. Work by Yebra et al. [6–8] focused on estimation of copper and rosin reaction rates in precisely calibrated model binders, including modelling of seawater and copper speciation within the coating leached layer, and produced accurate predictions of copper leaching rate and concentration profile in the leached layer. The authors highlighted the extreme difficulty in producing a global model for prediction of biocide leaching, noting that subtle changes in the binder composition would render the model inaccurate. Furthermore, the mechanics of delivery for evenly dispersed organic biocides are likely to be substantially different, but remain relatively unstudied in this medium.

The mechanics of molecular diffusion in polymers are significantly more complex than in true solids, liquids or gases, owing to the medium's inherent physicochemical heterogeneity and variable conformation depending on temperature. Nonetheless, a good understanding of the key mechanics governing diffusion in polymers has been achieved in areas such as pharmaceutical applications for drug delivery, and in food packaging [9–12]. Direct monitoring and measurement of diffusion rates is a lengthy and arduous procedure, particularly when considering materials with a low release rate. Antifouling coatings, in particular, present a highly complex multicomponent system; in addition, water ingress occurs into these coatings in the marine environment, resulting in a degree of plasticisation of polymer chains. The inclusion of large pigment particles, whose size scales are often within an order of magnitude of the total binder thickness, renders the medium effectively

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Nomenclature

D	diffusion coefficient, $m^2\ s^{-1}$
E	Young's modulus, Pa
E_0	critical energy, J
h	Planck constant, $6.6261 \times 10^{-34}\ m^2\ kg\ s^{-1}$
h_0	initial height of transition state cavity, Å
k_B	Boltzmann constant, $1.381 \times 10^{-23}\ J\ K^{-1}$
$Q^{\dagger}/Q$	ratio of the partition function of the transition state to that of the reactant state
r_i^{RS}	initial reactant state cavity radius, Å
r_i^{TS}	initial transition state cavity radius, Å
r_ϕ^{RS}	reactant state cavity radius with respect to swelling, Å
r_ϕ^{TS}	transition state cavity radius with respect to swelling, Å
T_b	boiling point, K
T_g	glass transition temperature, °C or K
υ	Poisson's ratio
V_{def}	deformation potential, $kJ\ mol^{-1}$
V_{LJ}	Lennard–Jones potential, $kJ\ mol^{-1}$
V_0^{RS}	initial reactant state cavity volume, $Å^3$
V_0^{TS}	initial transition state cavity volume, $Å^3$
ε	well depth, K
σ	Lennard–Jones diameter, Å
μ	Lamé constant
ϕ	percentage volume increase of film from swelling

anisotropic. There is modelling and experimental evidence demonstrating the limitation of water ingress and diffusion below the pigment front in antifouling paints [5–7,13,14]. As a result, simplifications must be made in order to treat the system as a traditional one-dimensional diffusion problem. In any case, the investigation of the accuracy of the modified cavity jump diffusion model provides a logical first step towards a 'base', from which other more complex scenarios can be modelled. In particular, the addition of intermolecular interactions of the binder with the biocide or other coating ingredients (via first principles or Hansen parameters) and the implementation of a binder polishing rate would be relatively simple adjustments to the model. Alternatively, the inclusion of more complex hydrodynamic phenomena and pigment dissolution within the same model would represent longer term goals.

In summary, the present study aims to assess the suitability of the best-suited present literature models for prediction of the lifetimes of integrated compounds in antifouling coatings. Unfortunately, literature efforts in modelling of diffusion have focused primarily on amorphous polymers above the glass transition temperature [15–20]. Consideration of below T_g acrylic polymers is limited [21,22] and models designed to estimate penetrant diffusion in glassy polymers have been found to have a significant degree of error for penetrants whose size scale differs from that of the repeating monomer unit [23]. Despite these shortcomings these models have been applied to a various coatings in this current work, with some modification in an attempt to increase the accuracy for ternary and co-polymeric systems.

2. Materials and methodology

A terrestrially derived dibenzofuran, usnic acid (hereafter termed furan derivative, FD), was selected as a promising natural product for integration into simple model antifouling coatings [24]. Work was carried out herein to further our understanding of the biocide's leach rate and behaviour alongside other studies within the project. To allow corroboration of the model results, pMMA (T_g = 90–100 °C) and a commercial binder (containing approximately 40 vol.% rosin) were immersed from a pontoon into the sea for a 10 month period at National Oceanography Centre (NOC), UK. This is a tidal basin in the docks of Southampton Water. The seawater quality is typical of that found in industrial estuarine conditions. A biocide loading of 10 wt.% FD was incorporated into the coatings to achieve saturation in the polymer solution. Natural seawater exposure at 1 m depth was chosen to provide a realistic in-service environment and eliminate inhibition of diffusion by accumulation of the active ingredient in the leachant solution. Replicate samples were placed on the shaded back side of exposed boards which experienced no direct sunlight.

Identical pMMA coatings and CDP (a rosin-based controlled depletion polymer) coatings were also immersed for accelerated rotor testing (25 °C, 17 knots at the rotor drum periphery where all panels were attached, equivalent to 8.7 $m\ s^{-1}$) at TNO (Nederlandse Organisatie voor toegepast-natuurwetenschappelijk onderzoek) Maritime Material Performance Centre (Den Helder, the Netherlands) as described in Goodes et al. [14]. A 24 h static immersion period was observed before starting the accelerated testing, to allow stabilisation of coating water content. Rotor testing was intended to provide a realistic representation of 'in-service' conditions in terms of operational speed, whilst accelerating the kinetics of biocide depletion by maintaining a significantly higher temperature than would be encountered in most service locations. Owing to the complex hydrodynamics of the rotor cylinder within its tank, convection and turbulence are both likely to play a substantial role. In addition to the traditional antifouling binder types, a novel hydrolysable poly(triphenylmethacrylate)/butylacrylate (p(TrMA/BA)) coating (50:50 wt.% co-polymer) was also subjected to rotor testing only (this experimental coating was not prepared for the static immersion testing). Despite the use of a primer layer, the commercial CDP coating containing the additive separated from its primer within a day of immersion – during the 24 h static period – so it was not possible to analyse the amount of additive lost for comparison with other systems.

Aged coatings (i.e. those that were recovered after pontoon and rotor immersions) were analysed by taking multiple cryofracture cross-sections of paint chips, which were then thinly sliced with a microtome (in the case of rotor-aged samples) and by incremental polishing of cross-sectioned PVC panels with fine SiC paper down to 4000 grit (for pontoon-immersed samples). These were subjected to optical and fluorescence microscopy compared to identical unimmersed coatings as described in detail in Goodes et al. [14]. Finally, the water swelling (at saturation) of each of the polymer systems was determined gravimetrically at 18 °C. pMMA and CDP binders had a low water content of 1 vol.% whereas the p(TrMA/BA) co-polymer was characterised by its very high water content (10.1 vol.%). The addition of the natural product did not significantly affect water uptake. Distilled water was used for this step. The surprisingly high water sorption determined for the trityl copolymer film is discussed later.

2.1. Selection of model for estimation of natural product diffusion

The Gray-Weale model [21] was selected as the most promising for prediction of penetrant diffusion in below T_g polymers. This model is based on the calculation of critical energy required for cavity 'jumps' between gaps within the segments of glassy polymers. The activation energy required for each event depends on the deformation of side groups required to allow the penetrant molecule to bypass, and hence relies strongly on the estimation of molecular and cavity geometry. Estimation of the jump length is the basis for calculating bulk diffusion. The energy required for large penetrants to deform neighbouring side groups is higher, so their movement