A probabilistic model for estimation of ionically permeable inhomogeneities in polymer coatings

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A probabilistic model for estimation of ionically permeable inhomogeneities in polymer coatings

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Abstract

The mechanism of ionic conduction through polymer coatings has been investigated. The presence of highly permeable areas in the coating (designated as D type areas), impose an electrochemical inhomogeneity which is identified by change in the ionic resistance as measured by DC method. The effect of coating thickness was studied on D type behaviour of coatings. A structural model is proposed to explain the changes in conduction mechanism by variation of coating thickness. Statistical models based on numerical (simulation-based) and analytical (probabilistic model) analysis of D type areas distribution have been advanced to estimate the number of D areas in any given coating based on the percentage of D type. Using these models the number of permeable (D type) areas can be estimated based on the D type percentage of the coating.

Keywords: Ionic conduction; Electrochemical inhomogeneity; Distribution model; Estimation; D type behaviour.

1. Introduction

Early studies of Bacon, Smith and Rugg \cite{1} revealed the significance of ionic conduction for protective properties of organic coatings. It was observed that a coating that maintained a resistance of
$10^8$ Ohm cm$^2$ provided good corrosion protection while one whose resistance fell below $10^6$ Ohm cm$^2$ did not. Since that time, ionic resistance has been used as a major criterion for determining the corrosion protection afforded by an organic coating [2–5]. Later studies revealed a bimodal mechanism of ionic conduction through polymer films [6–8] and determined the presence of highly permeable areas that form a small fraction of the coating. These domains are observed to be significantly more permeable than the bulk of polymer film to ionic species such as chloride [9] and increase in number and permittivity as the coating absorbs water [10]. Two distinct forms of conduction have been identified [11] for coating films which are of thickness typically used for individual coats in paint coatings (30-100µm). The first is I, or inverse type conduction, where the resistance of the film runs inverse to that of the solution. The second mode of through-film transport is named D, or direct type conduction where the film’s resistance follows that of the external solution. D type areas were found to be randomly distributed in organic coatings [12,13] while the conduction mechanism that was operative had a major influence on the corrosion protection afforded by the coating [4] to mild steel in strong chloride solutions. Further studies [14–16] revealed that under-film corrosion initially occurs at D type areas and then spreads from the interface as initiated by cathodic disbonding. It has been also shown that the mechanism of ionic conduction and local inhomogeneity of the polymer film plays a major role in the failure mode of protective coatings [17–21]. One of the major causes of formation of D type areas is believed to be the presence of regions of low crosslinking density within the film [22]. The beneficial effect of increasing crosslinking density of polymer on lowering the porosity and permeability has been shown by Worsley et al. [18].

A series of studies investigated the effect of electrolyte [11], temperature [23], pigmentation [24], polymer type [25–27] and solvent [22,28] on the D/I type ratio of paint film. Detached paint films were typically produced by applying the paint on a glass substrate after which they were dried in a glove box with airflow across the samples followed by soaking in water to allow removal of the film. Samples were stoved for two days at 60°C then mounted in small U shape glass cells exposing 1cm$^2$ to solution. The two arms of each cell were filled with either 3.5 M KCl solution or 0.001M KCl solution. Resistance was measured using a high impedance DC resistance electrometer. The number of D type samples divided by number of I types gives the D to I type ratio. A commonly used alternative term is the %D type which is defined as the number of pieces exhibiting D type behaviour divided by the number of pieces examined (D + I). It was postulated that D type areas only occupy a small fraction of a 1cm$^2$ film but this area has a remarkably higher permeability thus dominates the protective properties of the coating. It was also suggested that the water activity plays a key role in ionic conduction through I type coatings whilst the ionic strength controls the transport through D type coatings. In the latter case the barrier presented by the polymer to ionic movement is remarkably smaller, although less small than if D areas were caused by pores filled with the external electrolyte [11]. Among the parameters influencing ionic permittivity of polymeric coatings, coating thickness
has been shown to play a major role in determining the dominant conduction mode. This is manifested by increasing I type behaviour and ionic resistance as the film thickness increases [29,30].

Theories about the causes of D areas or D type regions have been advanced including solvent entrapment and dead (non-functional) molecules [4,15,22,31]. A third and new theory being proposed here is the Turing morphogenesis mathematical theory [32] applied to formation of cross linked molecules [33]. Certain types of dynamic systems (e.g. the cross linking process occurring in a polymer) which are initially homogeneous undergo a progressive change which leads to the appearance of spatial heterogeneity. This occurs due to an instability of the homogeneous equilibrium, which is triggered by random disturbances. The minimum of two substances are required to initiate a chemical reaction, e.g. oxygen and the reactive alkyd polymer or amide and epoxide compounds in an epoxy/polyamide system. The concentration of one species is dynamically maintained by a balance between the generation process whose rate is controlled by its concentration (e.g. the number of reactive double bonds in the alkyd resin), and its destruction process (e.g. once the cross link forms). The second species e.g. intermediate radical species, being formed at a rate mainly determined by the concentration of the first species and being destroyed by a rate proportional to its own concentration given that there be movement from one point to the other according to the laws of diffusion. For further information and mathematical representation of the theory see reference [32].

In the present paper, the effect of coating thickness on the electrochemical inhomogeneity, i.e. D type area, is investigated. Based on the experimental results and the wisdom received from previous works, a structural model has been proposed for the influence of coating thickness on the mechanism of ionic conduction in polymer coatings. Statistical-based models were utilized to express the number and distribution of D areas in a given polymer coating.

2. Experimental

2.1 Materials

The alkyd varnish was based on a short oil soya based alkyd resin with 40% v/v solid content in xylene supplied by Pronto Industrial Paints Ltd. A typical soya bean oil is composed of linoleic (54%), linolenic (5%), oleic (30%), palmitic (9%), stearic (4%) and arachic (1%) acids that are esterified with polyols (e.g. glycerol) and polyacids (e.g. phthalic anhydride or maleic anhydride) to form alkyd (alcohol-acid) polymer. The resulting polymer contains C=C bonds owing to the unsaturated fatty acids; linoleic, linolenic and oleic acids. The polymer is crosslinked through its C=C bonds in the air by an oxidative radical co-polymerisation. Solvent free epoxy paint was a two pack epoxy/polyamide system supplied by AkzoNobel International Paints with 100% solids content.
KCl was analytical grade from Sigma.

2.2 Methods

2.2.1 Sample preparation
Detached films were obtained by applying the liquid varnish on a non-stick PTFE (Polytetrafluoroethylene) sheet using a spreader bar as film applicator. The spreader bar has a precisely machined gap that lays down a film with the desired thickness and creates a very uniform film under optimum conditions. Dried films were then carefully delaminated from the PTFE sheet and the coating thickness was measured using a Defelsko PosiTest DFT thickness gauge. All coatings were prepared at Room Temperature (RT), i.e. 18-22°C. All films were left at RT at least for one week before testing.

2.2.2 Measuring D type percentage
%D type was determined by measuring the DC resistance of 3.2 cm² area (Note that it is three times larger than earlier Cambridge work which was conducted on 1cm² samples) detached coatings using a 610C solid state Keithley electrometer. Detached films were cut into approx. 4cm² squares and mounted in U shape glass cell (Figure 1) where the DC resistance could be measured in a two electrode arrangement across the coating using two saturated calomel electrodes (SCE). Keithley electrometer in ohms measuring mode measures the voltage drop across the sample galvanostatically with a current being driven through the sample. The current is reciprocal of the ohms scale set for the measurement, e.g. on 10⁸ ohms scale the current is 10 nanoamps. This results in a direct measure of resistance except when the sample itself generates a voltage. Here a simple subtraction method between two different ohm scales can be used to calculate the resistance. If the resistance of the sample is very high there will be significant voltage drop across the sample where the current is only very small. If the resistance of the sample is low a correspondingly larger current will be needed to obtain an observable voltage drop. Hence in use it is a minimum current instrument which is a significant advantage in making the measurement as non-destructive as possible while still being able to measure accurately very high resistances in a very short time scale. The SCE impedances, typically in the order of 10⁴ ohm is negligible compared to high impedance of organic coatings and therefore considered insignificant. This method of impedance measurement has been used and described in the literature a number of times [14,25,34]. The DC resistance was measured with first 1 mM KCl and then 3.5 M KCl solutions to identify the conduction type of each piece. KCl is the same salt used at the same concentrations as in the previous work conducted at Cambridge [7,14]. If the resistance was
lower in the 3.5M solution than that in 1 mM solution the sample was classified as a D type. If resistance was higher in the 3.5M solution than that in the 1 mM solution it was classified as I type. Coatings were in contact with each solution for at least 2 hours before the measurements were made. All measurements were performed at room temperature, 18-22°C. Subsequently %D type was statistically calculated for 20 samples as the number of D types observed divided by the total number of samples, i.e. 20. It should be noted that while resistance measurement on the attached coating (coating/metal substrate) system is also possible, the bimodal behaviour of coatings when exposed to different concentrations of salt solution is more pronounced and easier to detect when it is measured for a free film. When DC resistance is measured on a coating/metal substrate system, the bimodal behaviour is harder to detect due to other impedances interfering with the ionic resistance of organic coating such as the charge transfer and polarisation resistance at the metal substrate.

Figure 1 Experimental set-up for identifying conduction mechanism, i.e. D or I, of coating films.

3 Results and discussion

3.1 Effect of thickness

Results of DC resistance measurement for eighty nine, 3.2 cm² alkyd film samples with varying thickness are presented in Figures 2 and 3. Samples were classified as D or I type based on the resistance exhibited in 1 mM KCl and 3.5 M KCl. Figure 2 shows resistance values for D and I type films in 1 mM KCl and Figure 3 shown resistance values for the same D and I type films in 3.5 M
KCl solution. Figures 2b and 3b show there is an increase of resistance of D type films in both solutions as a function of coating thickness identified by the solid arrow. This can be explained by the longer conduction pathway as the coating thickness increases. The distribution in the “W” direction shown by the broken arrow in Figures 2b and 3b, is most likely attributed to the different number and sizes of D areas within samples [35]. Figure 2a and 3a indicate that I type resistance is much less dependent on coating thickness. Previous work [25] showed that resistance was approximately linearly proportional to thickness for I type films.

Figure 2 Distribution of resistance of I and D type alkyd films in 3.5 M KCl solutions.

Figure 3 Distribution of resistance of I and D type alkyd films in 1 mM KCl solutions.

Figure 4 shows the results of %D type measurement (based on twenty measurements) as a function of coating thickness for an alkyd varnish and a solvent free epoxy/polyamide paint. Increasing the
thickness enhances the homogeneity and leads to a greater probability of I type behaviour in any individual 3.2 cm\(^2\) area of coating. The presence of an ionically conducting continuous aqueous pathway is the essential requirement for D type behaviour. Therefore, thickening the polymer layer can potentially block or interrupt the conduction by much less permeable polymeric regions (e.g. regions of higher cross linking density). Earlier studies [36,37] based on measuring activation energy of different phases suggest that ionic conduction and water activity are much higher within a D type region compared to an I type region which showed dielectric type behaviour; but not as high as ionic conduction and water activity in a 100% aqueous environment. The structural model presented in Figure 5 explains the formation of D type areas and how they disappear by increasing the film thickness. A similar structural model had been proposed by Kendig and Leidheiser [16] for inhomogeneous permeation of electrolyte through a polymeric film towards a metal substrate and formation of conducting phase within the polymer film. The permittivity of a polymer film is significantly higher within the intermolecular cavities and local domains of lower crosslinking density. As these domains connect, they may form a continuous easy pathway for ions (Figure 5a) where a relatively large volume of water can be accommodated; thus the ionic activity of solution defines the electrical resistance (characteristic of D type areas). By increasing the film thickness there will be higher chance of interruption of pathway by a very much more insulating phase resulting in lower permittivity and I type behaviour (Figure 5b).

**Figure 4** Effect of thickness on alkyd varnish, solvent base epoxy/polyamide paint and solvent free epoxy/polyamide paint coatings based on the percentage of D and I type (from twenty samples each with 3.2 cm\(^2\) area).
Figure 5 Structural model for formation of continuous ionic pathways by adjoining the more permeable domains (a) and interruption of continuous pathways by much less permeable domains due to increasing the film thickness (b).

3.2 Numerical model

It has been found that increasing the thickness of the coating lowers the % D type. However measuring the % D type by using film samples with large size, e.g. 3.2 cm² in this work or 1cm² in Cambridge work, compared with the D areas within them does not quantify the number of D areas that are known to have <10μm size in diameter [10,35,38,39] and are the potential sites of corrosion initiation. Several assumptions should be made in order to translate the concept of variable ionic conduction into a mathematical model. First and foremost is the random distribution of D areas. This has been frequently shown elsewhere [12,13,34] and could arise as a result of the theory of morphogenesis being applied to the cross linking process.(see introduction) It has been suggested that distribution of D type areas obeys the Poisson model with a random distribution [30]. In the original work [30], % D type was measured for a number of groups of coating, each group consisting of 20 samples. All samples were made from the same type of coating, e.g. alkyd, with similar thickness. The %D type calculated for these groups of samples were not always the same but the values varied around a mean value with a Gaussian or Normal distribution when measured for several of groups of 20. Also a critical assumption here is that D areas are only a small fraction of the film. The very small
size of D areas explains the similarity of resistance of D type and I type films at low concentration of salt.

In order to simulate D areas distribution, a probabilistic-based random field from spatial statistics perspective is used. Nature of a homogeneous latent process, such as D areas distribution, can be numerically modelled with a randomised pattern via an appropriate point process [40,41]. Thus, to replicate a realisation of distributed D areas numerically, several random process of D areas in a two-dimensional plane with varying number of D areas were generated using the “homogeneous Poisson process” within “R” statistical computing platform [42]. Figure 6 shows three examples of such data generations for a certain case of 20 D areas distributed in a 10x10 area with 2x2 gridding (note that the values of lengths are dimensionless). % D type for these examples are calculated as 64% for Figure 6a, 56% for Figure 6b and 48% for Figure 6c. It is obvious that choosing a smaller sample size, e.g. 1x1, would result in a lower % D type for a given number of D areas. To obtain a repeatable mean value, a large number of these examples, i.e. 100, 500 and 1000, were generated and the average % D type was calculated using a Monte Carlo simulation model. % D type was defined as fraction of squares containing one or more D areas ×100. Using the Monte Carlo simulation model and an infinite number of data generations for each given number of D areas and mesh size would result in virtually zero error for each % D type calculation. The mesh size here is equal to sample size and is defined by the level of gridding of the entire surface. However, in practice with a limited number of samples, increasing the number of simulated samples would improve the graph resolution. This can be seen in Figures 7-9 where less “noisy” plots are produced by increasing the number of simulations from 100 to 500 and then to 1000.

**Figure 6** Three random distributions of 20 D areas in a two-dimensional plane generated using “Poisson point pattern”. Numbers in each square represent the number of D areas.
The resulting %D type for a given number of D areas and mesh (sample) size had a normal or Gaussian distribution around a mean value. The mean value was taken as the average % D type and plotted against the number of D areas for each given sample size. This process was repeated for varying number of D areas distributed in a 10x10 area with varying mesh size (gridding). Note that using a dimensionless window size brings about the possibility of applying the model to different size of samples, e.g. 10×10 m², 10×10 dm², 10×10 cm² etc. Figures 7-9 plot the number of D areas against %D type for different size of samples (gridding). Each curve in Figures 7-9 was generated for a given gridding or mesh size as demonstrated on the plot. This nomogram can be used to estimate the number of D areas in a larger surface based on the %D type measured in the lab. For example in a 100 cm² coating with 50% D type behaviour based on measurement with sample size of 1 cm² about 65 D areas are expected to exist. In fact %D type can be measured on a few samples, e.g. 20 samples, and the result can be extrapolated for a larger surface using the nomograms presented here. This is due to the important assumption of random distribution of D area. Therefore a smaller group of samples, e.g. 20, would be a statistical representative of the larger group. The significance of D areas has been defined earlier as potential sites of corrosion initiation. Nomograms such as presented in Figure 6-8 also bring about the flexibility of using different size of samples and yet results can be normalized for a direct comparison. It should be noted that all converted values extracted from these plots are statistical expected values and the values obtained from experimental measurements may vary within the standard deviation around the expected value.
Figure 7 Simulation-based estimation plots for number of D areas, up to 300 D areas, in a 10x10 area of coating based on the % D type and the sample size – 100 simulation replications

Figure 8 Simulation-based estimation plots for number of D areas, up to 300 D areas, in a 10x10 area of coating based on the % D type and the sample size – 500 simulation replications
Figure 9 Simulation-based estimation plots for number of D areas, up to 300 D areas, in a 10x10 area of coating based on the % D type and the sample size - 1000 simulation replications.

3.3 Mathematical model

Despite the general usefulness of simulation-based nomograms, they are relatively hard to generate and each individual graph will accommodate a limited number of D areas and sample sizes. Therefore, further effort has been made to draw a universal mathematical model for use with any given number of D area and size of samples. Generally, a point process $N$ is used to describe data that are localized in a bounded (finite) area $W$, where $W$ has a functional form. A homogeneous Poisson point process, $N$, in this area consists of $n$ points, $x_1, ..., x_n$, that are randomly located where points are uniformly and independently distributed in each dimension of $W$ [40]. The main assumption in a homogenous Poisson point process is that the number of points of process $N$ in area $W$ follows a Poisson distribution with a functional mean $\lambda(W)$ where $\lambda$ is called the intensity or point density of the process. This describes the expected mean number of points or D areas to be found in the observed area.

For the purpose of mathematical modelling, the sample size was represented by $d$ as the gridding level, e.g. $d=20$ means the entire surface was divided equally to 20 sections as in Figure 6. Assuming defects’ location as points in the area $W$ (see Figure 6), having at least one defect in one of the $d$-areas is the basic definition of D type behaviour and can be probabilistically modelled by a binomial distribution associated with defect proportion $p = d^{-1}$ and the intensity $\lambda$, as the unknown parameters. Thus, the probability distribution function (PDF) of having $X = \{x_1, x_2, ..., x_n\}$ defects in a $d$-area is obtained by equation (1):

$$
\Pr(X = x) = \frac{\lambda^x}{x! (\lambda-x)!} p^x (1-p)^{\lambda-x} ; \ x = 0, ..., \lambda. \quad (1)
$$

Assuming the above PDF, probability of having at least one defect in $d$-area is given by equation (2):

$$
\Pr(X \geq 1) = 1 - \Pr(X = 0) = 1 - \frac{\lambda^0}{0! (\lambda-0)!} p^0 (1-p)^{\lambda-0} = 1 - (1-p)^{\lambda} = 1 - \left(1 - \frac{d^{-1}}{d}\right)^\lambda. \quad (2)
$$

where $\Pr(X \geq 1)$ is the %D type, $\lambda$ is the number of D areas and $d$ defines the gridding level. In order to return an estimate of $\lambda$, equation (2) can be rearranged and represented as equation (3):

$$
\lambda = \log(1 - \Pr(X \geq 1))/\log\left(\frac{d^{-1}}{d}\right) \quad (3)
$$
Figure 10 illustrates a nomogram generated using equation (2) with sample sizes similar to simulated-based model (Figures 7-9) for up to 300 D areas. It shows an exact match between the simulated-based model and the mathematical model and indicates that equation (2) can be used as a universal model for estimation of number of D areas in a coating with a given %D type.

**Figure 10** Analytic estimation plots for number of D areas, up to 300 D areas, in a 10x10 area of coating based on the % D type and the sample size.

In order to provide a practical example for applicability of this mathematical (global) model to real experimental data, using equation (3) for the experimental data presented in Figure 4, the estimated number of D areas for the alkyl and epoxy coatings have been calculated and presented as a function of coating thickness in Figure 11.
4. Conclusion

A structural model has been proposed for the mechanism of ionic conduction in polymeric coatings and the effect of thickness on D type behaviour. The model works on the assumption that conductive pathways form by interconnecting small domains of higher permittivity such as local domains of lower crosslinking density. Increasing the thickness of coating increases the chance of blockage of the ionic pathways by impermeable polymeric phases such as domains of higher crosslinking density.

Statistical models were developed using two independent methods including generating simulated samples containing D areas and the mathematical modelling. Results showed an exact match between the two models and confirmed that they can be used for estimation of number of D area in a polymer coating with a given %D type. These models can be used to predict the number of potential sites of corrosion initiation under the coating which has a direct relationship with the protective properties of an organic coating.

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