Mechanism of ionic conduction in multi-layer polymeric films studied via electrochemical measurement and theoretical modelling

*Sina S. Jamali *[a], Thomas Suesse *[b], Safa Jamali [c], Douglas J. Mills [d], Yue Zhao [a]*

[a] ARC Research Hub for Australian Steel Manufacturing, Faculty of Engineering & Information Sciences, University of Wollongong, Wollongong, NSW 2522 Australia.

[b] National Institute for Applied Statistics Research Australia, Faculty of Engineering & Information Sciences, University of Wollongong, Wollongong, NSW 2522 Australia.

[c] Department of Chemical Engineering, Massachusetts Institute of Technology (MIT), Massachusetts Avenue, Cambridge MA, USA

[d] School of Science and Technology, University of Northampton, St George's Avenue,

Northampton, NN2 6JD, UK.

* Corresponding author: sjamali@uow.edu.au

ABSTRACT

Ionically permeable domains in polymeric protective coatings have been investigated empirically and theoretically. In the first part of the paper, results from recent experiments both complement and show agreement with received knowledge. This has allowed a physical model to be proposed for the mechanism of ionic conduction in polymeric coatings. This model assumes the random scattering of small regions with very different physical and chemical properties, akin almost to separate phase. Particularly the much higher rate of conduction is likely to have an impact on the coating's anti-corrosion ability. Based on the superimposition of permeable and impermeable domains, the model can be applied to allow comparison of multi-layer systems with single coat films of the same thickness. Such a statistical model has practical corollaries and in the second part of the paper statistical methods are advanced to allow determination of the probability of having these permeable domains in two, three, four and more coats. This has been further refined by a virtual simulation process using the distribution of permeable domains on a two dimensional plane. The significance of the theoretical models is then discussed with respect to the experimental data and what they mean in terms of protective ability.

KEYWORDS:
Electrochemical inhomogeneity; polymeric film; Ionic conduction; Theoretical modelling; protective coating.

1. INTRODUCTION

Inhomogeneity is an intrinsic aspect of organic coatings caused by variation in chemical and physical structure such as variation in film thickness, changes in local pigment volume concentration, deviations in film cross-link density (curing) and differences in chemical composition [1,2]. In cross-linking coatings there appears to be a certain type of inhomogeneity which influences strongly the ionic conduction through the coating. Owing to the marked difference in ionic conduction between these inhomogeneities and the bulk of the polymer, these areas are considered to constitute a separate phase. Unlike most other types of structural inhomogeneity, the size and nature of these domains means that they cannot be examined using routine microscopy and scanning techniques. They can however be detected electrochemically [3] due to the fact that they produce two distinctly different modes of ionic conduction through the coating. The “D” type mode represents Direct type conduction where the conduction follows that of the external solution (ionic conduction increases by increasing the ionic content of the solution). The “I” type mode represents Inverse type conduction, where the conduction in the film runs inverse to that of the solution. It has been suggested that the water activity plays the key role in ionic conduction through I type domains whilst it is the ionic strength that controls the transport of ions through D type domains where the size of conduction pathway is remarkably bigger [3]. Further studies [4,5] revealed that under-film corrosion initially occurs at D type areas and then spreads across the interface.

A series of studies investigated the effect of electrolyte [3], temperature [6], pigmentation [7] and solvent [8] on I and D type conduction and /or the D to I ratio of paint films. Some of this work indicated that, despite D type areas occupying only a small fraction of the coating, these areas have a remarkably higher permeability thus dominating the protective properties of the coating [9]. Fluorescence microscopy [10,11] on epoxy coating has indicated that following exposure to NaCl, water and chloride ions are clustered in discrete sites of up to 10µm in size on the surface of epoxy. Other works [14, 15] have demonstrated the significance of electrochemical inhomogeneity on the mechanism of under-film corrosion as well as loss of adhesion in the long term exposure test [16]. Attempts to examine inhomogeneity of nano-structure of polymer coatings using routine microscopy techniques such as SEM [14] and scanning probe techniques [15,16] only reveal the micro/nano-structure of the very surface of a coating. More localised information about distribution of D type in a single or multi-layer coating can be obtained using a wire-beam multi-electrode [17,18]. However this only enabled the identifying of D type containing parts of coating within a few mm^2 area which is still several orders of magnitude larger than the probable size of most individual D areas.

Given the assumption that D areas are small, discrete and randomly distributed, theoretical modelling can be applied and become a reliable tool for understanding the heterogeneous structure of organic coating and its formation due to inhomogeneous chemical reactions, physical phenomena and network defects [19,20]. In a recent study [21] such a statistical modelling approach was implemented to estimate the number of D areas in an organic coating and a physical model was proposed for formation of D areas in a coating film based on formation of conductive pathways by interconnecting small domains of higher permittivity such as local domains of lower crosslinking density. The effect of increasing thickness in increasing electrochemical homogeneity was explained by the increasing distance that the ion has to travel increasing the chance of blockage of the ionic pathways by impermeable polymeric phases such as domains of higher crosslinking density. The aim of this present study is to explore inhomogeneity and D type behaviour in a multi-layer coating system both empirically and theoretically. Also the possibility of estimating the size of D type areas via a theoretical model is investigated.

2. EXPERIMENTAL SECTION AND PHYSICAL MODEL

2.1 METHODS AND MATERIALS

2.1.1 Materials

The alkyd varnish was based on a short oil soya based alkyd resin with 40% v/v solid content supplied by Pronto Industrial Paints Ltd, Derbyshire, UK. The solvent was Xylene. The varnish was used as-received without further filtration. In order to obtain the detached film, the liquid resin was applied onto a non-stick PTFE surface using a spreader bar with appropriate gap size to produce a single coat of dry film thickness (DFT) of 85μm (±5μm). It carefully delaminated after it was fully cured. The coating thickness was then measured by a Defelsko PosiTest DFT gauge. The triple layer alkyd varnish was prepared via a layer by layer procedure to produce a final film thickness of 85±5 μm composed of three 25-30 μm coats. Second and third layers were applied after the former layer was fully cured. Also a thicker single coat 110 μm alkyd film was produced. All coatings were prepared at Room Temperature, i.e. 18-22°C, and allowed to dry naturally for at least two weeks before being tested.

2.1.2 Methods

The determination of D or I type behaviour and %D type was carried out according to the procedure detailed in previous publications [18,21]. Twenty pieces of film were cut out and mounted within U shape glass cells. Then each was classified as I or D type by measuring its resistance in contact first with 1 mM KCl and then in 3.5 M KCl. Samples were assigned as D type when the DC resistance decreased by changing solution from 1 mM KCl to 3.5 M KCl. Samples were assigned as I type when the DC resistance increased by changing solution from 1 mM KCl to 3.5 M KCl. DC resistance of the films in contact with 3.5 M KCl was taken as either the R_D or R_I. The number of pieces giving D type behaviour divided by the total number of pieces produced the figure for the %D type. The value of ionic resistance for I types, i.e. R_I, was generally high (typically 10^{10}-10^{12} ohms/cm^2) while R_D was much lower (typically 10^6–10^8 ohms.cm^2). A solid-state Keithley electrometer model 610C was used for DC measurement of coating resistances. The area of each piece of coating was 3.1 cm^2 area.

Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC model 821 at 5ºC heating rate within the range of -10ºC to 150ºC under N_2 atmosphere. Standard 40 µL crucible aluminium pans were used and the weight of samples was 8-12 mg. Samples were cut from fully cured detached films. Data presented here are normalized in regard to the weight of samples.

Dynamical thermo-mechanical analysis (DMTA) experiments were performed by a DMA Tritec 2000, Triton-technology at 5 ºC/min heating rate, 1 Hz oscillation under 1 N force and 20 µm displacement. Storage and loss modulus were measured within the temperature range of 5 to 65ºC. Specimens were rectangular detached films with a fixed length of 11 mm and approximate width of 6.5 mm fixed to a single cantilever with tension mode. Tg was determined at the maximum of the α transition peak of the tanδ.

2.2. ELECTROCHEMICAL RESULTS

Figure 1 compares the %D type and %I type of the detached piece of triple coat alkyd (85±5 µm) with a single coat of the same thickness. The three coat is 100% I type (0% D type) whereas the single coat alkyd is only 50% I type (50% D type). This implies that the three coat system is more electrochemically homogeneous. The I type behaviour and electrochemical homogeneity are in fact synonyms herein, i.e. the more electrochemical homogeneity the higher %I type and this means fewer D type area. It is noteworthy that the triple layer coating is also more electrochemically homogeneous than the alkyd coating with an even higher film thickness of 110 µm. This superior homogeneity could be due to better solvent removal when the layers are applied as a number of thin films. Or it could be a result of the D areas being very small compared with the I Area and hence the D area is very likely to be overlaid by an I type area in subsequent layers. A similar explanation was proposed for higher impedance of double layer phenolic resin compared to that of the single layer [17].

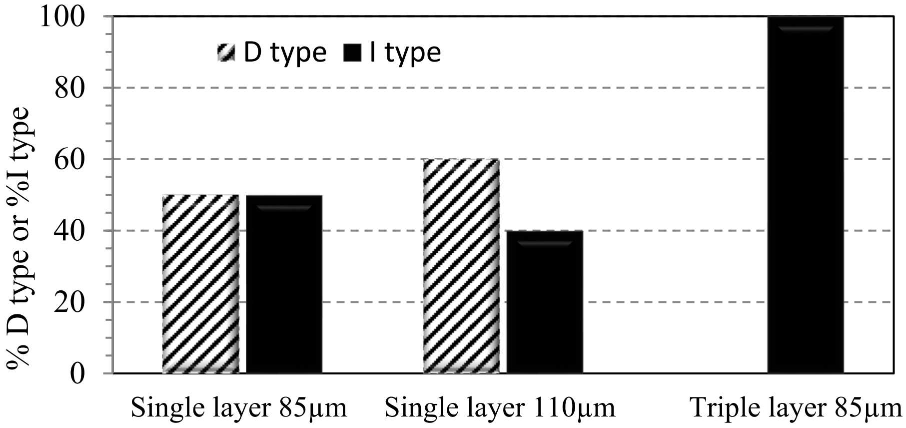

Figure 1. Effect of multi-coat application on D/I type behaviour of 85±5 µm alkyd. The %D type and %I type were calculated based on 20 specimens of coating in each group, each specimen with the surface area of 3.1 cm^2.

2.3 COMPARISON WITH EARLIER ELECTROCHEMICAL RESULTS

Results of the early study on thickness and number of layers [4] are summarised in Table 1. Note the thickness of double layer coatings in the case of alkyd and tung oil varnishes (60-65µm) is not equal to either of the single layer coatings and yet the double layer system at 75µm produces significantly fewer D types than the single layer films with even higher thickness values (85µm). The significant impact of thickness in reducing the number of D areas has been shown in several other independent studies [17,18,21].

Table 1. Summarized results of an early study comparing %D type in single and double coat alkyd, tung oil and epoxy films (data reproduced from ref [4]).

Number of coats	Varnish type	Thickness µm	%D type
1	Alkyd	40-45	52 %
1	Alkyd	75	10 %
1	Tung oil	35-40	72 %
1	Tung oil	85	25 %

1	Epoxy	35-40	77%
1	Epoxy	75-80	45 %
2	Alkyd	60-65	5 %
2	Tung oil	60-65	2.5 %
2	Epoxy	70-75	2.5 %

2.4 PHYSICO-MECHANICAL ANALYSIS

DSC results obtained from the single 85µm alkyd film and the triple coat (composed of three 30µm coats) alkyd film when both wet and dry the latter being prepared by submerging the detached films in de-ionized water for 24 hr are shown in Figure 2. The reason for examining wet films was because it has been suggested that the water activity plays the key role in ionic conduction through I type coatings whilst the ionic strength controls the transport through D type coatings [22]. Hence DSC measurement on wet films are expected to more sensitively differentiate between a predominantly I type film and a film with several D type areas.

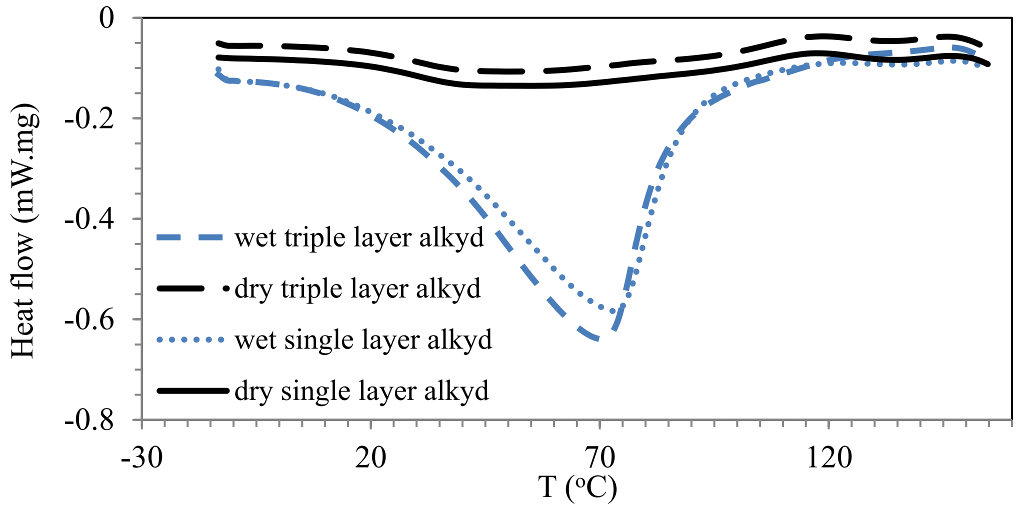

Figure 2. DSC thermograms of wet and dry films of single and triple layer alkyd varnishes.

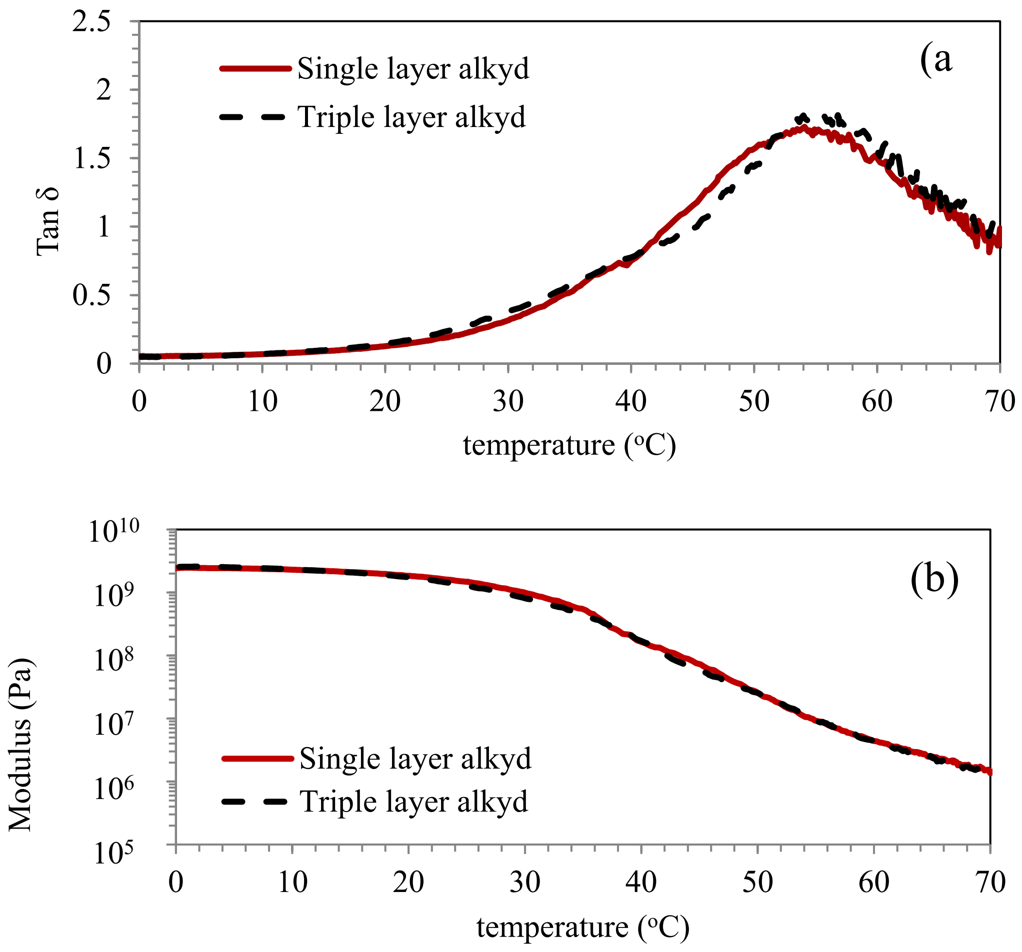

Figure 3. DMA of single and triple layer alkyd varnishes. (a) storage modulus and (b) tan δ. Measurements were conducted with 10μm displacement at 1 Hz in tension mode.

Figure 3 shows the DMTA results, i.e. Tan δ (a) and Modulus (b), obtained from the single coat and three coat films. Both samples, i.e. single layer and triple layer alkyd films, were dry film without exposure to electrolyte. Neither the DMTA nor the DSC results show any significant difference in the curves. This implies no significant difference in the homogeneity level in terms of cross linking between the single and multi-layer alkyd films at the same thickness.

2.5 DISCUSSION

One of the possible mechanisms responsible for this superior homogeneity of multi-layer coating compared with single coat at the same thickness is solvent retention. This can significantly change the permeability of a coating. Once the solvent has evaporated from the top layer of alkyd film, a viscous layer will form on the top via oxidative crosslinking while considerable amount of solvent is still present in the lower section of the film [23]. In this case, the entrapped solvent evaporates through the crosslinked top layer over time leaving "solvent escape ways". Multi-layer application with thin individual layers, in theory, can reduce the chance of solvent entrapment thus enhancing homogeneity of coating. An alternative (or contributing) explanation is that multi-layer application may increase the crosslinking density by providing more accessible oxygen to each individual layer for oxidative drying. This would render the actual structure of the three separate layers to be more homogeneous than the structure of the single layer. If either of these explanations were correct it would be expected that a difference in the DMTA and DSC results would be seen. Although it is not possible to completely disprove or prove this hypothesis from the DSC and DMTA results, nonetheless the results shown in Figures 2 and 3 are not supportive of either of the mechanisms being the main cause of the observed difference in electrochemical homogeneity between single and multi-layer alkyd films. If indeed there is variation in cross-linking density and/or presence of "solvent escape ways" this can only be in a very small proportion of the coating, such that the bulk of physical and mechanical properties are not varied. It is noteworthy that neither of the DSC and DMTA have shown the capacity and the required sensitivity to capture and characterize D type behaviour which further necessitates the need for theoretical modelling of such behaviour as currently the only viable tool for better understanding of this phase in the coating film.

An alternative explanation is that the D areas, are very small compared with the I area. This means that they are very likely to be overlaid by an I type area in subsequent layers. A similar explanation was proposed for higher impedance of double layer phenolic resin compared to that of the single layer [17]. This is in agreement with the earlier assumption that D type areas are only a few tens of microns in size [11,24–26] and supports the hypothesis for superimposition of small D type areas on the large I type area and blockage of the D type passage in the coating being the mechanism responsible for the remarkable homogeneity (I type characteristic) of multi-layer coating.

2.6 Proposed Physical Model

The model presented in Figure 4 illustrates this proposed mechanism. A continuous ionic pathway may form if the pathways or D type areas in the individual layers line up. Given that D type areas are very small and form only a small fraction of the coating, there is only a small probability of D areas lining up to form a through pathway. In section 3 theoretical models have been developed in order to investigate this probability quantitatively. This physical model is also consistent with the localized reactivity concept and the associated physical model for distribution of D areas proposed by Kendig and Leidheiser [27].

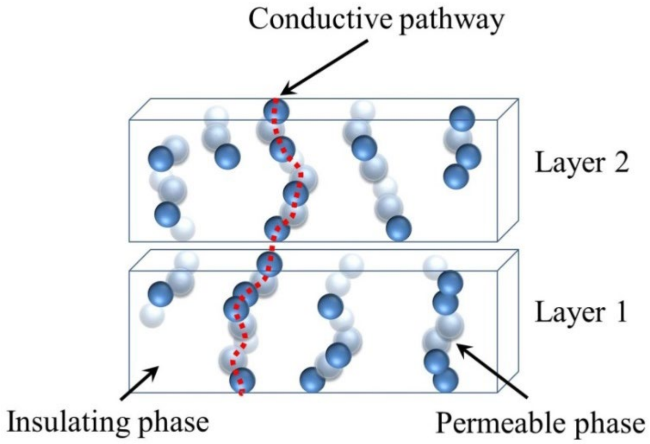

Figure 4. Schematic physical model for blockage of D type areas by superimposition on the impermeable I types in a multi-layer coating.

3 THEORETICAL MODELLING OF D AREAS

Taking the explanation that D areas are small and randomly distributed [18,28,29] allows statistical analysis to be conducted in order to estimate the chance of forming a continuous D type channel in a multi-layer coating as proposed in Figure 4. This model has important practical ramifications when a coating is applied on a very large surface and there is a need to be able to predict how many D areas exist in the coating. The significance of D areas as potential sites of corrosion initiation has been demonstrated in earlier studies [4,5]. It has been suggested that random distribution of D type areas obeys the Poisson model. This random distribution can be shown to arise if the theory of morphogenesis is applied to the chemical and/ physical processes which create the dried film Subsequently this gives rise to inhomogeneities in a coating [30] and these are critical to its protection ability.

3.1 Mathematical model

In the following, simplifying assumptions have been made to allow derivation of an approximate mathematical model which provides explicit formulae for the key variables. It is assumed that each layer is divided into a number of pixels (small areas) on a rectangular basis, for example *i*) 10,000 by 10,000 or *ii*) 1,000 by 1,000 pixels. Results in the section 3.2 are all generated based on a layer with 10^8 (10,000×10,000) pixels. Number of pixels were varied in section 3.3 for studying the size of D areas. For simplicity the number of pixels of each layer is assumed to be the same and denoted by N. In each layer the number of expected pixels that represent D areas is denoted by m with $0 \leq m \leq N$. Although D type areas have never been observed and their actual shape is unknown, assuming a square shape for D areas may well be unrealistic. However from a theoretical point of view with respect to the hypothesis presented herein, the shape of D areas (either square or circle) does not make a significant difference. These pixels are simply 2 dimensional areas that produce a pathway once they overlap. A homogenous Poisson point process for the number of D areas is assumed where m is the intensity or point density of D areas [31]. In each layer n pixels, $x_1,\ldots,x_n$ representing D areas, are randomly and independently distributed. The term K represents the number of layers. For one layer (K=1) the expected number of D areas is m pixels out of N total pixels.

When the number of layers is increased to K=2, then an overall D area for a particular pixel only occurs if both layers have a D area at the exact same pixel (see the physical model in Figure 4). Similarly when K>2, then an overall D area at a particular location/pixel only occurs if all layers contain defect at the same location.

The effect of increasing the number of layers to K>1 on the expected number of overall D areas M_K , is explored. For example when 1,000 D areas are expected per layer, (m=1000) it is important to know how this translates to the overall number of D areas for two or three layers. Ideally an increase in K will dramatically decrease M_K so that the multi-layer coating exhibits a homogeneous

I type behaviour and affords a high level of corrosion protection. The aim of the mathematical model is to obtain accurate but simple formulae for M_K for given m and K. Also the probability of having no overall D type area, denoted by $P_{0,K}$, has been calculated.

Detailed mathematical derivation of the formula for probability of j total D areas is given in the supplementary material-Appendix A. Equation (1) for $P_{j,K} = P(X=j)$ allows the calculation of the probability for the presence of j number of D areas in the multi-layer coating for any given number of layers of coating, K, and any given number of D areas per layer, m.

$$P_{j,K} = \binom{m}{j} \sum_{l=0}^{m} (-1)^l \binom{m-j}{l} \left[\frac{\binom{m}{j+l}}{\binom{N}{j+l}} \right]^{K-1} \qquad (1)$$

Equation (1) can be simplified for j=0 to equation (1a) for zero D areas in the multi-layer coating. The notation $\binom{m}{j} = \frac{m!}{j!(m-j)!}$ is the well-known binomial coefficient.

$$P_{0,K} = \sum_{l=0}^{m} (-1)^l \binom{m}{l} \left[\frac{\binom{m}{l}}{\binom{N}{l}} \right]^{K-1} \qquad (1a)$$

Both the general $P_{j,K}$ and $P_{0,K}$ can be difficult to calculate for very large N and m, as the binomial coefficients are difficult to obtain. Based on $P_{j,K}$, the expected number of overall defects, M_K , for K layers can be derived. Detail of the derivation is given in supplementary material-Appendix B which results in a rather simple form for M_K presented in equation 2.

$$M_K = m \left(\frac{m}{N} \right)^{K-1} \qquad (2)$$

Note, the equation 2 can be simplified to $M_1 = m$ when K=1.

To obtain a simpler formula for $P_{0,K}$, a lower bound $\tilde{P}_{0,K}$ can be derived such as defined in equation (3). Detail of derivation is given in supplementary material-Appendix C.

$$P_{0,K} \geq \tilde{P}_{0,K} = 1 - m \left(\frac{m}{N} \right)^{K-1} \qquad (3)$$

This formula is particularly useful to ensure that $\tilde{P}_{0,K}$ is larger than a certain threshold. For example if the aim is to have $P_{0,K} \geq 95\% = \tilde{P}_{0,K}$ (probability of having zero D area is more than

95%) equation 3 enables the determination of K, the number of layers, such that $\tilde{P}_{0,K} = 95\%$. Rearranging equation 3 to calculate K results in equation (4).

$$K \geq \frac{\log\left(1 - \tilde{P}_{0,K}\right) - \log(m)}{\log(m) - \log(N)}, \quad (4)$$

where log is the natural logarithm. However any other logarithm can also be used, such as log_{10}.

3.2 *Model based on virtual data simulation: probability of D areas in multi-coat films*

Data simulation has been conducted to assess the accuracy of the above mathematical formulae and also the accuracy of the lower bound $\tilde{P}_{0,K}$, First, results are presented for the expected number of overall defects, E(X), in Figures 6-8. Values calculated using equation 2 are shown in black. These are compared with the average number of overall D areas over many simulated data sets. For simplicity the number of D areas per layer is held constant and equal to m. The generation of data and the calculation of P(X=0) and E(X) was done with the statistical computing software R [32]. For each layer the number of D areas was fixed and equal to m and randomly m out of N pixels were chosen as the distribution of D areas. Then for each pixel it was checked whether the D areas in all layers lined-up to result in an overall D area. Then the total number of overall D areas was recorded. Overall 2,000 such simulated data sets were generated for each value of m and K and the average number of overall D areas was used as an estimator of the true E(X).

The number of expected (statistically) D areas for a two layer film system has been calculated and given in Figures 6. Results for three, four, five, six and seven layer systems are also calculated and given in supplementary material-appendix D. Figure 7 summarizes Figures 6 & D1-D5 with showing graphically how the number of D areas in a multi-layer film vary as the number of layers and number of D areas in individual layers increase. In simple words, Figures 6 & D1-D5 indicate that the higher the value of m is, the larger is also the value of M. However effectively m stays near zero until it reaches a threshold from which M increases sharply. It is also noteworthy that these theoretical models are dimensionless and therefore any size of specimen and any speculated dimension for the size of D area can be examined. For example, given $N=10^8$, in the case of a 100 cm^2 overall size of coating sample, pixels will translate into D type areas with 10μm×10μm squares. Although presence of 10^6 D areas in a 100 cm^2 coating is highly unlikely, the plot had to be extended such far to exhibit at what point D areas overlapping start to make a significant difference. These results indicate that the number of expected D areas reduce by around 100 fold by addition of each extra layer. They also show that values acquired from virtual simulation are very close to those obtained from mathematical formula which further validates the Equation 2.

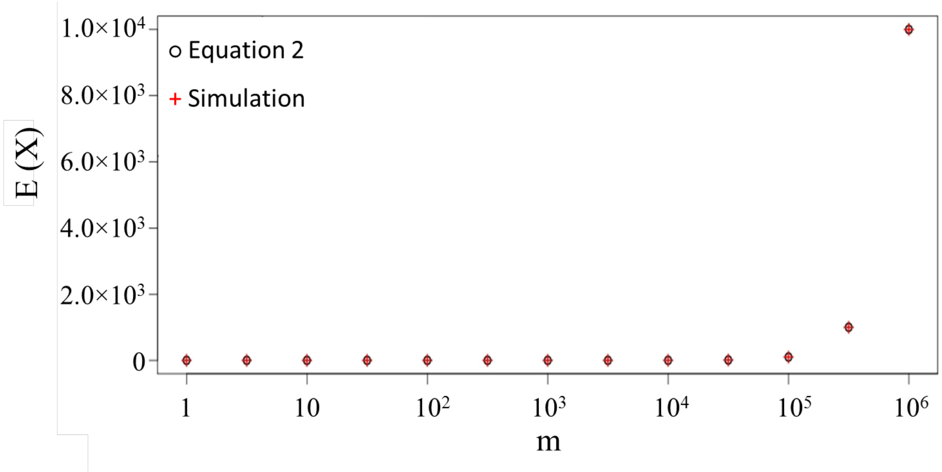

Figure 6. Expected number of overall D areas, E(X), in a two layer coating system vs. number of D areas in individual layers, m.

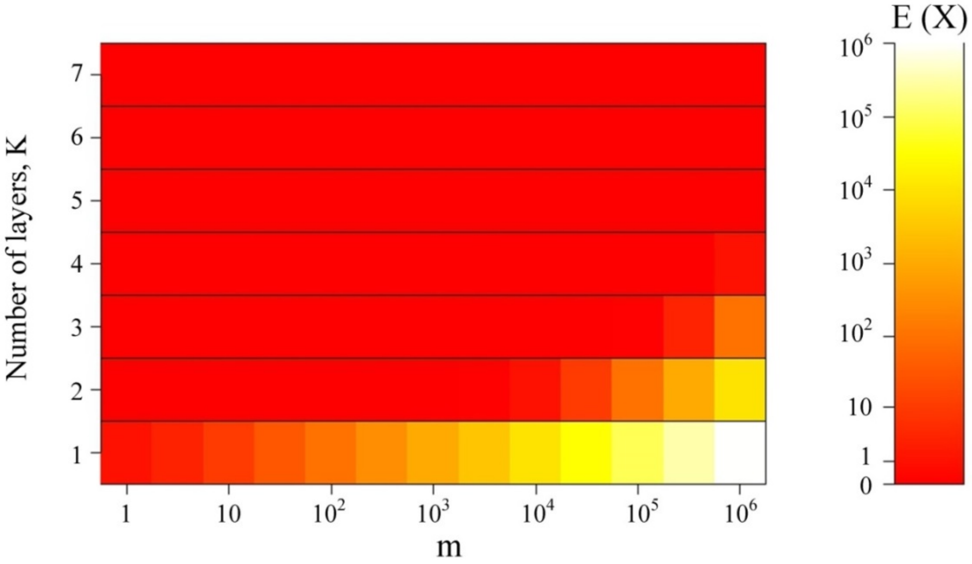

Figure 7. Number of layers, K vs. number of D areas in individual layers (m) for N=10^8 (i.e. 10,000×10,000) showing how number of overall D areas, E(X), practically reduces to zero beyond layer 4.

Figure 8 demonstrate the probability of having zero D area, $P(X = 0)$in a two layer film system with varying number of D areas in individual layers. Results for a three, four, five, six and seven layer film have also been produced and given in supplementary material-appendix E. The values of $P(X = 0)$ have been calculated based on the lower bound (black), global formula or equation 1 (blue) and the estimated $P(X = 0)$ by simulation (red). Herein when m increases the $P(X = 0)$ stays near 1 and from a certain value of m, this probability decreases sharply until it reaches zero. The global formula, Equation 1a, becomes numerically unstable for large m and N (Figure E.4 and E.5) and the lower bound formula, Equation 3, is a more suitable approximation in these cases. It is noteworthy that the $P(X=0)$ does not change significantly by increasing the number of layers from five to six or further to seven. A probability of slightly less than 1 can be seen at $m=10^6$ (an extreme case for number of D areas) in $K=5$ but for all other values in a five, six and seven layer system, the $P(X=0)$ is practically 1. Figure 9 summarizes Figures 8 & E1-E5 graphically by showing how $P(X=0)$ changes by increasing the number of layers and number of D areas in individual single layers simultaneously. It is noteworthy that $P(X=0)$ is a very important parameter particularly from a practical point of view. It can be used to estimate how many layers with a given thickness should be applied on a certain metal surface to ensure (with 95% confidence) no D area exists. This will have a remarkable impact on the anti-corrosion characteristics and service life of the coating.

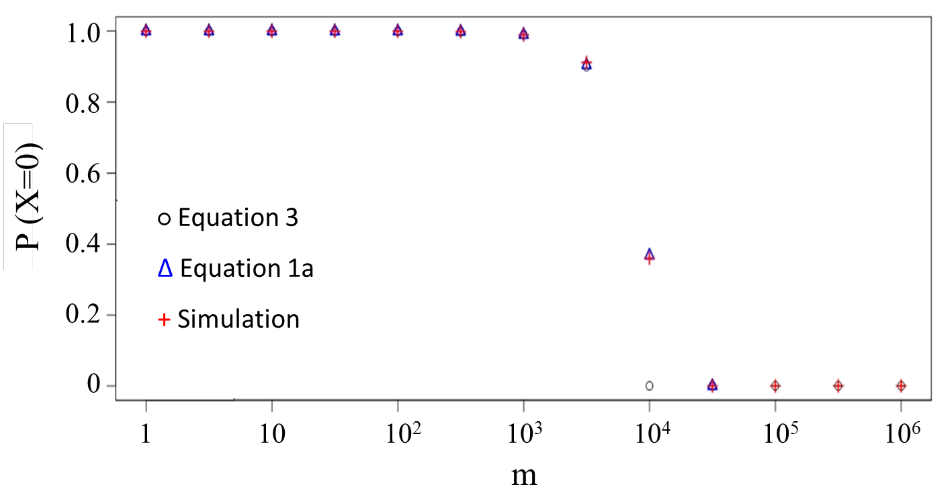

Figure 8. Probability of zero overall D areas in a two layer coating system $P(X=0)_{95}$ vs. number of D areas in individual layers (m).

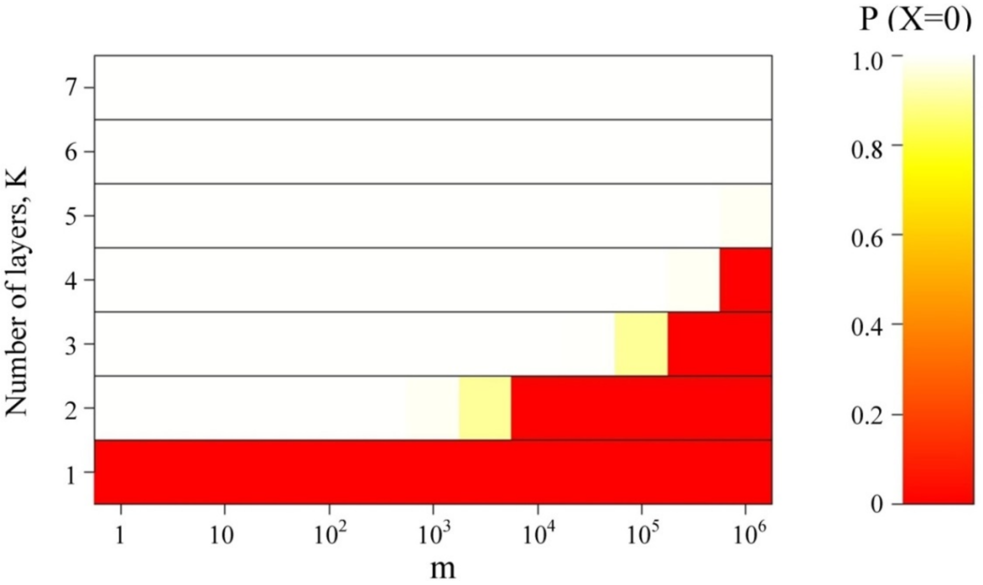

Figure 9. Number of layers, K, vs. number of D areas in individual layers, m, for N=10^8 showing how probability of zero overall D areas rapidly increases as the number of layers increases.

3.3 Model based on data simulation and real data: Size of D areas

In order to estimate the size of D areas we need to plot E(X) against varying N (mesh or pixel size) for a fixed m (number of D areas) and K (number of layers) and consider which N matches real laboratory data. It should be noted that the size of D areas can be (and most likely are) different between coatings with different chemistry. This is based on the hypothesis that the curing mechanism (e.g. oxidative drying in alkyds, ring-opening in epoxy, radical polymerization in polyesters etc), presence of solvent, non-functional (dead) polymer chains and other factors still unknown, all have an impact on the formation of D areas.

Herein we consider the case of epoxy coating with the %D type results presented in table 1. Using nomograms presented in the previous study [21] for 77% D type in 35-40μm thick epoxy, the number of D type areas in a 10×10 plane is calculated to be around 150. The %D type for the double layer epoxy with thickness of 70-75μm was 2.5% (i.e. one D type coating in the 40 specimens that were examined) which translates into 2.5 D areas. To model the size of D areas, the E(X) is plotted in Figure 10 against varying N for m=150 and K=2. Figure 10 indicates that for 2.5 D areas the N should be larger than 10^4 or in other words the size of D areas must be smaller than 1mm^2. The model also will not produce useful data if applied to coatings with 100% I type characteristic such as the data presented in Figure 2, simply because the number of D type areas will be zero in the multi-layer system regardless of N. In fact, in order for this model to work properly and to obtain a more realistic N, a large data base is required to maximize signal/noise ratio and to improve accuracy of the estimation. Figure 11 presents the P(X=0) for the epoxy coating with *m*=150 and *K*=2 and indicates a high confidence for absence of D type areas when *N* reaches 10^6. This again translates to D areas with 100µm×100µm size which of the same order as the speculated size of D areas.

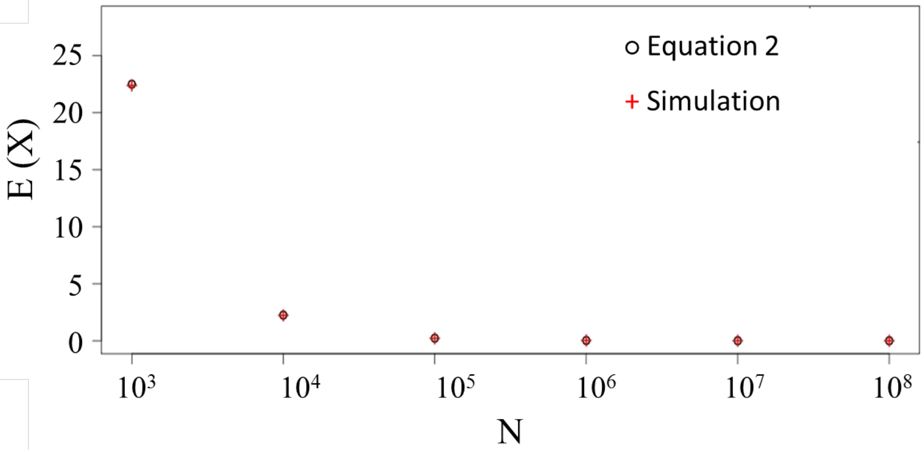

Figure 10. Expected number of D areas, E(X), vs. size of D areas, N, in a two layer film for a fixed number of 150 D areas number per individual single layer.

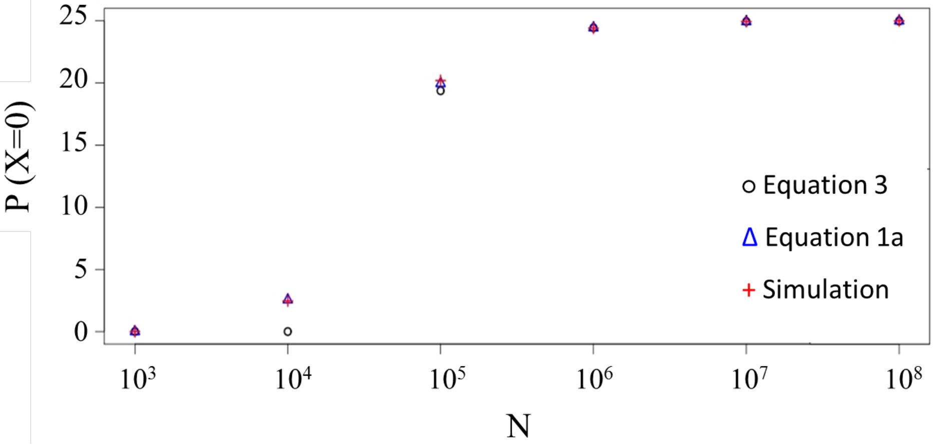

Figure 11. Probability of zero overall D areas, P(X=0) vs. size of D areas, N, in a two layer film for a fixed number of 150 D areas per individual single layer.

4 CONCLUSIONS

Highly homogeneous and I type behaviour of a triple-layer alkyd coating was demonstrated and compared to a single layer alkyd coating with inhomogeneous electrochemical characteristic. However structural changes and enhancement in homogeneity associated with easier removal of solvent or enhanced cross linking could not be detected by bulk physico-mechanical techniques (i.e. DSC & DMTA). It was hence concluded that the D type sites where the structural changes significantly occurred must be very small in size. By treating D areas as small, discrete and randomly distributed within the area of a coating, a structural model was proposed for blockage of D type areas in a coating by I type area from a second layer when two individual coating films are superimposed.

Following on from that, a theoretical model based on probabilistic and combinatorial principles, such as the inclusion/exclusion principle [33] was developed. Such a model enabled the derivation of closed form formulae based on simple assumptions, such as independence of layers and pixels. The simulations were done with a statistical computing software [32] in order to assess the accuracy of the theoretical formulae. It was shown that the number of D areas reduces by about 100 fold as a result of one additional layer in the coating system. And that in a four coat system for most common cross linking systems the number of D areas is effectively reduced to zero.

In practice and from a commercial point of view, this goes a long way to explaining what has been known since at least the late 19th Century that it is more economical to apply several thin layers of coating rather than a very thick single coat. Multi-coat application synergistically reduces the cost of material as well as number of D areas as potential sites of corrosion initiation.

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