



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

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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.

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 10 μm 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-

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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 mm² 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 85 μm ($\pm 5 \mu\text{m}$). 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 $\pm 5 \mu\text{m}$ 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/cm²) while R_D was much lower (typically 10^6 – 10^8 ohms cm²). 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 cm² area.

Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC model 821 at 5 °C heating rate within the range of –10 °C to 150 °C under N₂ 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

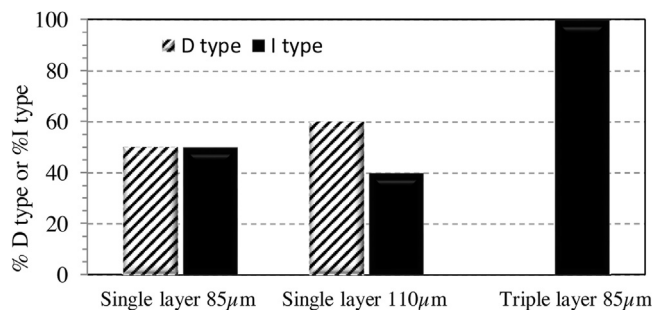


Fig. 1. Effect of multi-coat application on D/I type behaviour of 85 $\pm 5 \mu\text{m}$ alkyd. The % D type and %I type were calculated based on 20 specimens of coating in each group, each specimen with the surface area of 3.1 cm².

presented here are normalized in regard to the weight of samples.

Dynamical thermo-mechanical analysis (DMTA) experiments were performed by a DMA Triton 2000, Triton-technology at 5 °C/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 5–65 °C. 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. T_g was determined at the maximum of the α transition peak of the tan δ .

2.2. Electrochemical results

Fig. 1 compares the %D type and %I type of the detached piece of triple coat alkyd (85 $\pm 5 \mu\text{m}$) 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].

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 (60–65 μm) is not equal to either of the single layer coatings and yet the double layer system at 75 μm produces significantly fewer D types than the single layer films

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%

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