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THE ROLE OF COMPUTED TOMOGRAPHY IN UNDERSTANDING INHIBITOR RELEASE FROM COATINGS

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SUMMARY: The mechanism of inhibitor release from coatings containing corrosion inhibitors is important in many industries from aerospace to infrastructure. Models of release often assume Fickian diffusion and treat the polymer matrix as a medium through which this occurs. However, the details of structures within coatings including those based on polymer structures, inorganic particles (such as fillers) and inhibitors is poorly explored. X-ray and backscattered electron computed tomography (X-ray CT and BSE-CT respectively) based on a variety of techniques are revealing the rich variety of structures that exist with paint coatings and shedding new light on transport mechanisms within these coatings. X-ray CT can be based on a range of different measurements including the most commonly used probe of X-ray absorption and to a lesser extent backscattered electron contrast. This paper provides an overview of the use of some of these types of techniques in investigating paint structure for pipeline coatings.

Keywords: Protective Coatings, Corrosion Inhibitors, Inhibitor Leaching, Pipeline Coatings, Aerospace Coatings.

1. INTRODUCTION

Increasing access to a range of X-ray sources has seen a huge expansion in the use of computed tomography (CT)-based techniques for many applications. Materials science is one area where CT-based techniques are being used more extensively; this includes coatings [1-6] as well as the microstructure and corrosion of metals [7-10]. 3D reconstructions based on diamond ultramicrotomy where backscatter electron images are collected at each slice has also had a big impact on characterisation of coatings and metal microstructures and corrosion of the latter [11-13] and atom probe tomography has been used to study nanostructure in some metals [14-17].

In the coatings area, recent studies have shown the complexity of structures within coatings [7]. These include different densities of polymer as well as extended structures related to the inorganic compounds such as fillers, extenders and inhibitors. In the case of the polymer components it has become clear that different density epoxy can be formed in coatings. These structures are thought to be related to crosslinking density of the polymer and are presumably related to the I and D type polymer regions that were reported some years ago [18] which lead to differential properties of coatings [19]. In the case of inhibitor particles in coatings, it has recently been shown they can form connected networks which have a fractal dimension [5, 20]. The release of inhibitor from these structures has been shown to be through the void structures created by the inhibitor dissolution. This process is proposed to start at the surface of the coating and penetrates into the body of the coating. In the written paper

we present 3-dimensional reconstructions of the polymeric and inorganic components of a high build epoxy coating and characterise the internal structures that are present in the coating. In the oral presentation this approach to studying internal structure is extended to the structures formed by inhibitor particles and how these influence inhibitor release.

2. EXPERIMENTAL DETAILS

2.1 Coatings

The coating studied in this work is a two-part, high build epoxy used in the pipeline industry. It is an amine-cured epoxy comprising major fillers of calcium carbonate (CaCO₃), silica (SiO₂) and talc, small amounts of organophilic clay and titanium oxide, among other components (Table 1) [21, 22]. The resin and the hardener of the coating were mixed together in the ratio 3 to 1 by volume. It was then applied on the steel plates using a Sheen drawdown applicator. The average dry film thickness selected for all the experiments was 230 μ m. The coating was allowed to cure for at least one week under ambient conditions, before further experiments could be carried out.

Resin		Hardener	
Ingredients	%	Ingredients	%
poxy Resin	15-40	N-Aminoethvlpiperazine	40-70
Calcium Carbonate	15-40	Epoxy Novolac Resin	15-40
Talc	15-40	Nonyl Phenol	10-30
Bisphenol F Epoxy	10-30	Amino Silane	3-7
Aliphatic Glycidyl Ether	3-7	Bisphenol "A"	3-7
Orqanophillic Clay	1-5	Polyfunctional Aziridine	3-7
Titanium Dioxide	1-5		
Phenyl Carbinol	1-5		
Fumed Silica	0.5-1.5		
Orqanophilic Clay	0.5-1.5		
Propylene Carbonate	0.5-1.5		

Table 1. Composition of high build epoxy coating used in this work

2.2 X-ray computed tomography and Data Constrained Modelling

Slithers of the coatings examined were in the configuration presented in Figure 1 to generate the CT data. The samples chosen were either in the "as prepared" or plastically strained to an elongation of 2.5% with and without expose to NaCI (0.6g/L) electrolyte for 27 days. In the case of plastically strained samples these were coatings on a C450 stainless steel and the plastic strain refers to the C450SS. For each coating two sets of X-ray absorption projection images were acquired at 16 keV and 24 keV X-ray photon energies respectively at the BL13W beamline in Shanghai Synchrotron Radiation Facility (SSRF). For each projection the exposure time was 4 seconds at 16 keV and 24 keV each such that in every projection image set, there are 900 projections. Between every 50 projections, there are 2 flat-field images. The acquisition of the dark-field images was carried out in the instant before as well as after the required dataset. For an effective pixel size of 650nm, optics were positioned in front of the detector CCD so as to get a 10x magnification. The X-TRACT software was used for the reconstruction of the tomographic slices. The reconstruction included a Paganin's phase retrieval algorithm followed by the filtered back-projection of the parallel X-ray beam [23].



Figure 1 Schematic for sample configuration for data collection

Then the computation and visualization of the organic, inorganic, and void components in the structure was done by the DCM software. The DCM technique enables the investigation of a system consisting of more than one component with the help of X-ray CT data so as to achieve a 3D compositional distribution [1, 3, 24-27]. The stack of two dimensional X-ray CT slices is used by the DCM software to reconstruct this 3D structure, which is comprised of voxels (three dimensional units on a simple cubic grid) A voxel is represented by the volume-fractions of coating constituents, namely polymer, fillers, and voids. Practically, this means that different components of the system (polymer, fillers, and voids) which have different linear absorption coefficients, can be separated from other components of the coating. Intuitive 3D visualization of a given component is performed by adjusting the voxel volume-fraction to opacity relationship.

3. RESULTS

Figure 2 shows a backscattered electron (BSE) image collected from a cross section of the coating as well as an image combining four elemental maps from the same cross section. The white arrow in the BSE image points to residual flaws in the coating. The red colour in the EDS map reflect CaCO₃ distribution as inferred from the Ca K α line. There are a range of clays in the coating (Table 1) which contain Mg (Mg K α line) and are indicated by the pale green colour while the SiO₂ particles (Si K α) are indicated by the blue colour and small TiO₂ (Ti K α Line) are indicated by the purple colour. It can been seen that the CaCO₃, talc, and SiO₂ particles are angular in shape and have a range of sizes from a few microns up to typically 20 microns, although there are a few larger particles. The TiO₂ particles are much smaller (typically a few microns) and rounded. All the inorganic phases are well dispersed in the epoxy coating. Figure 2 (right) shows a typical reconstruction of the distribution of large inorganic particles. However, because the linear absorption co-efficient of the CaCO₃, talc and SiO₂ particles are similar it is not possible to distinguish between them.



Figure 2: Left: Backscatter electron image of fillers in an epoxy-based coating used for pipelines. The white arrow points to residual flaws in the coating. Middle: Colour map based on EDS analyses for the different phases including CaCO₃ (red arrow), Talc (green arrow), SiO₂ (blue arrow) and TiO₂ (e.g. small particles in purple circle). Right DCM representation of inorganic particles within the epoxy (no distinction is made between the different types.

Figure 3 shows another analysed volume of the coating. The small number of inorganic particles within this volume are randomly distributed (Figure 3, left). The DCM representation of the different types of voids as well as different volumes of polymer density are also presented in Figure 3. The largest voids by volume in the coating are bubbles with each individual bubble represented by a different colour. An example of the bubble is the cream feature on the left face of the void cluster. It is surrounded by dense epoxy which apparently is further surrounded by a thin region of void (grey shell) that separates it from the medium density epoxy. Another type of void observed within the coatings is an extensive void network which represent areas of extremely low polymer density and, as will be discussed in more detail below, often lie at the interfaces with other components of the coating. The large, extended blue structure in Figure 3 (centre) is an example of a void network. On the right hand side of Figure 3 is the DCM representation of the polymer density. The majority of the polymer is of a similar density but there are regions of very high density (green) which, as mentioned above, can surround bubbles, as well as regions with much lower density (sienna and red colours) which will be discussed in more detail with respect to Figures 4 and 5.

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Figure 3: Inorganic particles in coating, void clusters including bubbles (each cluster in a different colour), and polymer density with legend.

The total combination of inorganic particles is shown in the red feature in Figure 4(a). The large inorganic particles are self evident, but the diffuse "cloud" within the epoxy represents the distribution of the very small particles of TiO₂. Another feature in Figure 3(a) is an apparent boundary volume around the larger inorganic particles in which the TiO₂ particles are excluded adding complexity to the heterogeneous structure of the coating and highlights how the DCM approaches provide detail that is not evident in 2D studies such as the EDS maps in Figure 2. In Figure 4(b), the inorganics have been combined with the epoxy components revealing some of the subtleties of the coating structure. It can be seen that the lower density epoxy sits between the TiO₂ particles and the other inorganic fillers at the interface between these two densities of epoxy. This suggests that TiO₂ and the other particles have some type of interaction with the epoxy system which will probably depend on surfactants, surface chemistry and surface charge of the TiO₂.



Inorganics CaCO₃, fumed SiO₂, Mg-clays and TiO₂ Polymer + inorganic fillers

Figure 4: Left: Inorganic components including the large particles comprising, $CaCO_3$, SiO_2 and Clays as well as diffuse distribution of TiO₂. These are all in red. Right: the combination of the inorganic components with the polymer component (colour coding is the same as for the polymer component in Figure 2).

Finally, Figure 5 shows the steps toward combining of all the different components. On the left is the void contribution which includes and extended network voids as well as bubbles surround by the high density epoxy component. In the centre is the polymer component showing the different density epoxy components. On the right is the combination of all these components as well as the inorganic component in red.. It can be seen that there are at least two independent, internal structures within the epoxy. The first is the structure around bubbles that includes the inner void of the bubble, which is encased in a sphere (approximately) of high density epoxy which itslef is surrounded by a void structure which separates it from the normal density epoxy. The second structure involves the inorganic particles and the epoxy.

Clearly, the presence of the inorganics influences the crosslinking of the epoxy since a lower density epoxy is created in their presence. The large inorganic particles such as the calcia, talc and silica particles appear to be at the "centre" of these regions and the TiO_2 particles from a boundary along with the extended void structure (blue) between this region and the normal density epoxy. Since this second structure extends throughout the coating it may have a significant influence on the mechanical and transport properties of the coating.



Figure 5: Plastically strained sample exposed to 0.6g/L NaCl for 27 days. Left: void clusters, Centre: polymer components and right: combination of inorganics, void components and polymer.

4. DISCUSSION

The data presented in this paper show that pipeline coatings have complex microstructures for the individual phases that form the coating. These include void structures, which, apart from bubbles, form at a number of different interfaces within the coating. The large inorganic particles adopt a different distribution to the diffuse distribution of the TiO₂ phase and the epoxy itself has a number of different densities most likely relating to the level of cross-linking. These different structures for each of the components combine to form two distinct substructures within the coating itself as described in the previous section. These are: (i) a structure around bubbles with involves dense epoxy, which is presumably heavily cross-linked which is separated from the average density epoxy by some void structure and (ii) the structures developed between the inorganic phases and the epoxy. In this second structure the large inorganic particles appear to be the nucleation sites for the formation of a volume of lower density epoxy surrounding the particle. From this data it is clear that the inorganics influence the polymerisation reaction, but it is not clear how it happens. It would seem that there are a few possibilities. First the particles themselves may act as polymerisation initiation sites. The second possibility might be that they reduce the level of amine available for cross linking. A third possibility may be that they influence the level of solvent in this region.

Both these networks represent heterogeneous structures within the coatings which could lead to differential properties of the coating including water and electrolyte uptake, mechanical structures and electrochemical properties.

5. CONCLUSIONS

In this study the data constrained modelling (DCM) approach was used to study the internal structure of pipeline coatings. It has been shown that the internal structure of epoxy-based coatings used in the pipeline industry is quite complex showing heterogeneous distributions of both polymer density as well internal structures involving the inorganic particles. These combine to make two substructures including (i) bubbles surround by a high density polymer shell and (ii) a low density epoxy network incorporating the inorganic particles which has an interface with the normal epoxy decorated by TiO₂ particles and a void network.

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