Understanding the effect of nanoporosity on optimizing the performance of self-healing materials for anti-corrosion applications

S Sellaiyan\textsuperscript{1,2}, S V Smith\textsuperscript{1}, A E Hughes\textsuperscript{3}, A Miller\textsuperscript{4}, D R Jenkins\textsuperscript{5} and A Uedono\textsuperscript{6}

Centres for Antimatter-Matter Studies (CAMS) at the \textsuperscript{1}Australian Nuclear Science and Technology Organisation (ANSTO) and the \textsuperscript{2}Australian National University. \textsuperscript{3}CSIRO Future Manufacturing Flagship, Clayton South MDC 3169. \textsuperscript{4}CSIRO Mathematical and Information Sciences, Glen Osmond, SA 5064. \textsuperscript{5}CSIRO Mathematical and Information Sciences, North Ryde NSW 1670. \textsuperscript{6}Institute of Applied Physics, University of Tsukuba, Ibaraki 305-8573, Japan

E-mail: svs@ansto.gov.au

Abstract. The chromate-based epoxy primer film was prepared on glass and metal surfaces using various graded doctor blades. The quality and consistency of the films was assessed using scanning electron microscopy and the porosity within the film characterized by positron annihilation lifetime spectroscopy. The positron lifetime ($\tau$) distribution for the epoxy polymer matrix was resolved using the CONTIN program. The free volume was found from the ortho-positronium component. The optimum thickness for the films was established for future structure/activity studies.

1. Introduction

Materials that have the ability to heal themselves are known as self-healing. They have the ability to restore the material to its original set of properties after thermal or mechanical damage. They can be metals, ceramics, polymers or their composites. One well known class of inhibited paints is the chromate based primers, which are still used in the most severe environments to protect a wide range of metallic substrates [1,2]. These types of coating systems are currently employed to protect a wide range of engineered structures from corrosion [3]. In the aerospace industry, alloys are selected for their superior ratio of weight to mechanical performance. However, they have poor corrosion resistance and films must be developed to protect them. These protective films are generally paint based incorporating chemical inhibitors that have the ability to prevent or slow corrosive processes. The inhibitor contains a leachable component (anti-corrosive pigment) that is released in order to prevent the corrosive reactions. The free volumes or voids are important properties to incorporate into the films for the inhibitor to work efficiently. We are interested to understand how porosity influences the ability of these films to repair themselves.

Positron annihilation lifetime spectroscopy (PALS) technique is a powerful characterization tool for the study of free volume sizes and free volume fraction in polymeric materials. The utility of the
positron in the study of polymers is enhanced by the fact that the positron can capture an electron and form a bound system called positronium. In polymers, the long lifetime component represents the formation of ortho-positronium, ortho-Ps, and it is this component that gives information on free volume characteristics within a material. Madani et al. [4] used PALS to characterize both dry and water-saturated epoxy systems incorporating a selection of non-chromate corrosion inhibitors. The same authors have studied voids at the interface between a SrCrO₄ inhibitor phase and an epoxy matrix using PALS [5]. While Cao et al. [6] examined primer/topcoat systems using Doppler broadening of energy spectroscopy (DBES), the mean implantation depth of the positrons was insufficient to provide any information about the primer layer.

The present study involves the use of PALS to determine the free volume or voids within the chromium doped primer (CP) paint films and establish the optimum thickness for future leaching studies.

2. Experimental

To the epikote 828 (1 g) (Epoxy resin produced from bisphenol A and epichlorohydrin, Resolution Performance Products) was added strontium chromate (0.5 g) followed by hardener 92133 (2.2 ml) (ANAC Advanced Coatings). The mixture was thoroughly mixed and then added to glass and Ni plate using a spatula. A range of films of various thicknesses (15, 22, 30 and 50 µm) on glass surface and a three layers thick film (100 µm thickness of each layer) on a Ni surface was prepared using various graded doctor blades.

The films were left to dry overnight and then characterized by Scanning Electron Microscope (SEM) and PALS. Morphology of chromium inhibited primer film were studied after platinum sputter coating with a scanning electron microscopy (ZEISS ultra plus SEM) at 10 kV accelerated voltage and 4 mm working distance. The lifetime spectra of positrons were measured using a conventional lifetime system (²²Na source, 10 µCi) with BaF₂ scintillators attached to H3378 (Hamamatsu Photonics) photomultiplier tubes and digital oscilloscope [7]. Each spectrum contained about 6 x10⁶ counts.

3. Result and Discussion

Many trials were performed to obtain a consistent and uniform coating of the chromium based primer. The weight percentage of substituents was optimized to epikote (29.2%), strontium chromate (14.6%) and hardener (56.2%). The mixture was then left (5-10 mins) at room temperature to thicken prior to coating on the substrate. A typical SEM of films produced is illustrated in Figure 1.

![Figure 1. SEM Micrographs of CP films at 5000 X magnification](image1)

![Figure 2. Positron lifetime spectra of 15, 30 and 300 µm thick CP films](image2)
Positron annihilation lifetime experiments were carried out on CP films deposited on glass plates (15, 22, 30 and 50 µm thick) and on Ni plates (300 µm thick). For the current study three different lifetime components were refined; \( \tau_1 \), \( \tau_2 \) and \( \tau_3 \), with relative intensities of \( I_1 \), \( I_2 \) and \( I_3 \) (proportional to the probability of each process). Figure 2 shows typical lifetime spectra of the chromium inhibiter primer films. After fitting the data using the CONTIN code [8], we observe three lifetime components and their intensity as shown in Figure 3. The first lifetime (\( \tau_1 \)) is the weight average between the lifetime of \( \text{para-Ps} \) (\( p \)-Ps) and the relatively short lifetime of positrons in the polymer, the second lifetime (\( \tau_2 \)) is the intermediate lifetime of the free positrons prior to annihilation by an electron and the longest lifetime (\( \tau_3 \)) is due to the \( o \)-Ps.

For CP films with thickness of 15-50 µm on glass, a proportion of the positrons annihilate in the substrate. The lifetime of this \( o \)-Ps annihilates component in the substrate was established to be 0.960 ± 0.006 ns with an intensity of 29 ± 1%. The \( \tau_3 \) value appeared to increase with increasing film thickness. This is because a higher proportion of \( o \)-Ps annihilated in the film instead of the substrate. For CP film with 50 µm thicknesses, however, the \( \tau_3 \) value seems to be saturated. The lifetime of positrons in polymer films were found to be \( \sim 2.1 \) ns. However because of the additional positron component from the glass substrate further work was conducted using nickel as the substrate.

For CP film (3 x 100 µm thickness deposited on nickel substrate) almost all positrons were found to annihilate in the CP film. Therefore the \( \tau_3 \) value observed could confidently be used to estimate the size of free volumes in the film. However as the film was multi-layered it is difficult to assess if the porosity occurs within each layer or between the layers. For the multi-layer film the \( \tau_3 \) value was optimised (2.12 ± 0.01 ns) using equation (1) to obtain mean free volume hole radius, \( R \), according to Tao 1972 and Eldrup et al. 1981 [9,10].

\[
\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1}
\]

where \( \tau_3 \) (o-Ps lifetime) and \( R \) (hole radius) are expressed in ns and nm, respectively. and \( R_0= R+\Delta R \) where \( \Delta R \) is a constant for an electron layer thickness (0.166 nm).

From this \( \tau_3 \) value the mean free volume pore radius \( R \) was estimated to be 0.29 nm. The free volume size (\( V_f \)) was then calculated (i.e. \( V_f = 4/3\pi R^3 \)) to be 0.11 nm³ within the film.

Dull et al. [11] have extended Tao-Eldrup model to calculate the rectangular pores from \( o \)-Ps lifetime. Further analysis of current data using the Dull model to determine free volume as a rectangular pore gave a similar R value of 0.30 nm.
The free volume hole distribution can be calculated for o-Ps lifetime using equation (2).

\[ S_{LT}(t) = \int_{\lambda=0}^{\infty} \lambda \alpha(\lambda)e^{-\lambda t} d\lambda \]  

(2)

where \( \lambda \) (the annihilation rate) is the reciprocal of lifetime \( \tau \) with an annihilation probability-density function (PDF) \( \lambda \alpha \).

The measured lifetime spectra were analyzed with a time resolution (full width at half-maximum) of approximately 170 ps by a numerical Laplace inversion technique [8]. Figure 4 gives a typical positron lifetime (\( \tau \)) with PDF distributions for the 300 \( \mu \)m thick CP film. The three peaks correlate to para-positronium (p-Ps), positron, and o-Ps annihilations components, respectively. The o-Ps lifetimes values were \( \sim 2.1 \) ns and are consistent with analysis reported above.

4. Conclusion

The chromate inhibited primer films were coated on glass and Ni substrate and analysed by PALS to determine optimum condition for future leaching studies. SEM show the films are consistent. The o-Ps component (\( \tau_{o}=2.12 \) ns) from the PALS data were fitted to determine pore shape. Optimum thickness for CP films was found to be above 50 \( \mu \)m thickness.

References

[1] Scholes F H, Furman S A, Hughes A E, Nikpour T, Wright N, Curtis P R , Macrae C M, Intem S, and Hill A J 2006 Prog. Org. Coat. 56 23
[2] Furman S A, Scholes F H, Hughes A E, and Lau D 2006 Prog. Org. Coat. 56 33
[3] Ghosh S K 2009 Self-healing Material: Fundamentals, Design Strategies, and Applications (Wiley-VCH Verlag GmbH & Co.KGaA)
[4] Madani M M, Miron R R, and Granata R D 1997 J. Coat. Technol. 69 45
[5] Madani M M, Miron R R, and Granata R D 1999 (ANTEC 99 New York) p 2202
[6] Cao H, Zhang R, Sundar C S, Yuan J P, He Y, Sreczki T C, Jean Y C, and Nielsen B 1998 Macromolecules 31 6627
[7] Saito H and Hyodo T 2003 Radiat. Phys. Chem. 68 431
[8] Gregory R B 1991 Nucl. Instrum. Methods Phys. Res. Sect. A 303 496
[9] Tao S J 1972 J. Chem. Phys. 56 5499
[10] Eldrup M, Lightbody D, Sherwood J N 1981 Chem. Phys. 63 51
[11] Dull T L, Frieze W E, Gidley D W, Sun J N, and Yee A F 2001 J. Phys. Chem. B 105 4657