Depth profiles and free volume in aircraft primer films

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Abstract. Positron annihilation lifetime spectroscopy (PALS) and associated techniques provide non-destructive methods to study the free volume inside polymeric materials, and to study material characteristics over a depth profile. Cast free films of organic- or aqueous-based, non-chromated aerospace primers, when cured for about one week, had very different water vapour transport (through-plane) behaviour. In addition, both types of primer films showed strong anisotropic behaviour in in-plane versus through-plane water vapour transport rates. We report the differences between the organic- and aqueous-based aircraft primer films samples and their surface depth profiles. In bulk PALS measurements, an aged, organic-based film exhibited typical lifetimes and intensities for a particulate-containing polymer film on both faces. In contrast, aqueous-based films exhibited face oriented-dependent differences. In all aqueous-based samples, the $I_3$ value of the back of the sample was smaller. The primer film samples were also evaluated with mono-energetic positron beam techniques to generate depth profile information. The heterogeneity in the samples was verified by Doppler broadening of energy spectroscopy (DBES). A model for the differences in the faces of the films, and their layered structure is discussed.

1. Introduction
Coatings used to inhibit corrosion of metal surfaces are complex mixtures comprised of polymer, molecular organic, pigments, inorganic particulate, and many other components [1]. Each component, along with any additives, plays a role in the physico-chemical structure, adhesion properties, and corrosion inhibition characteristics of a particular coating system. Typically, metal surfaces require a primer coat to enhance the adhesion performance of a subsequent or final coating system. Coatings may be generally classified into those with organic-based or aqueous-based carriers; another aspect is the addition of inhibitors to further mitigate corrosion at a coated surface.

It was previously found that a set of epoxy polyamide primers (one aqueous-based and one organic-based), with praseodymium inhibitor, exhibited differential water vapor transport rate behavior [2]. Water vapor transport is one critical aspect of corrosion formation under coatings. The aqueous-based primer (Deft-98) also showed an abnormal curing time dependent rate, while an organic-based primer (Deft-84) had almost no dependence on the curing time (after 7 days curing). The observation of dissimilar in-plane water vapor transport and curing time suggested further investigation using positron techniques. Positron annihilation spectroscopy (PAS) techniques provide a unique method for the structural and free volume evaluation of thin films, including heterogeneous coatings [3, 4].
2. Experimental
The details of the primer film samples’ provenance, preparation, and characteristics were previously reported [2]. A special arrangement was made to have samples evaluated by PAS at 7- and 21-day curing times for comparison to ‘aged’ samples (> 1 month). General positron annihilation techniques and methods have been reviewed and reported from this lab [5, 6].

2.1. Bulk PALS.
PALS bulk measurements were performed by using a conventional fast-fast coincidence method at 25 °C. The time resolution of the spectrometer was <300 ps, measured using a ⁶⁰Co source in the ²²Na energy window settings [7]. Samples were prepared as before [2] and used as received under ambient or vacuum (< 1 × 10⁻⁴ torr) conditions at specified curing times. A ²²NaCl positron source (sealed between Kapton disks) was sandwiched between two identical, double-stacked film samples (30 mm × 30 mm × 0.35 mm). The stacked samples (~ 0.7 mm total per side) assure that all source positrons annihilate within the samples (d ~ 1.6 g/cc). Further, the film samples were oriented with respect to their front face (the side open to atmosphere during curing) or their back face (substrate side). Positron interaction with the source coating is taken into account in the data analysis.

All PAL spectra were resolved into three components by using the PATFIT program [8, 9]. The spectra were then fitted to three exponential lifetime components: the component with the longest lifetime (τ₃ = 2.0–2.2 ns) and its relative intensity (I₃) is assigned to pick-off annihilation of o-Ps in the void spaces of the film. Since the variations of τ₁ and τ₂ are much less than that of τ₃, the observed lifetime of o-Ps (the triplet state of Ps) may be directly correlated to the size of free-volume holes [10, 11]. Bulk phenomena and radius distribution were also evaluated using the MELT software [12].

2.2. Monoenergetic Positron Beam PALS and DBES Depth Profiling.
2.2.1. Monoenergetic Positron Lifetime Analysis. Conventional PALS [13] at varied positron implantation energy (∝ depth) was used to measure the free volume properties in the coating film samples (~ 0.35 mm). PALS data contains quantitative information on the free-volume properties in polymeric systems from the surface, at interfaces, and into the bulk. For the slow positron beam at UMKC the lifetime resolution is ~500 ps for counting rates of 100-500 cps. Each PAL spectrum contained 1 million counts. The obtained PAL data were fit into lifetime components using the PATFIT program [8-9] and also into continuous lifetime distributions using MELT [12]. The smoothed lifetime distributions from MELT analysis are presented below.

![Figure 1](image-url)  
**Figure 1.** Representative positron annihilation lifetime spectra illustrating the differences between the front and back faces of the Deft-98, aqueous-base primer film, at 21-days. Lifetime spectra were taken under vacuum and ambient conditions.
2.2.2. Depth Profiling Using DBES. The S-parameter of Doppler broadening energy spectra (DBES) was measured as a function of implantation energy using the slow positron beam (0-30 keV) at the Positron Science Laboratory, Department of Chemistry, University of Missouri-Kansas City [14, 15]. A vacuum in the sample chamber was maintained between 10^{-7} and 10^{-8} torr. DBES spectra were recorded at r.t. as a function of positron energy from about 0 to 25 keV. The DBES spectra were measured using an HPGe Detector (EG&G Ortec with 35% efficiency and energy resolution of 1.5 keV at 511 keV peak) at a counting rate of approximately 2,500 cps. The total number of counts for each DBES spectrum was 2 million. The obtained DBES spectra were characterized by the S-parameter, defined as a ratio of integrated counts between the energies of 510.3 and 511.7 keV (S width) to the total counts after the background is properly subtracted. Since the S parameter represents the relative value of the low momentum part of positron-electron annihilation radiation, it is sensitive to the change of the positron and Positronium (Ps) states due to microstructural changes. The S parameter has been widely used in detecting free volume depth profile in polymeric systems [16-18].

3. Results and Discussion

After an initial experiment, bulk and beam PALS and DBES measurements were carried out considering the orientation of the film to the positron source. Thus, films were evaluated in a face-to-face or a back-to-back fashion in bulk measurements, and also before and after exposure to beam conditions (high vacuum and incident irradiation). ‘Front’ here means the top, exposed face of a film laid down for curing; ‘back’ means the surface contacting the substrate upon which the film was cast.

3.1. Bulk PALS evaluation of primer films.

The Deft-84 organic-based primer film (an aged sample) exhibited typical o-Ps lifetimes ($\tau_3$) and intensities ($I_3$) for a particulate-containing polymer film (data not shown). A comparison of the intensities ($I_3$) and estimated average pore sizes ($R$), for the organic-based films of either mixed faces or oriented faces indicated the relative homogeneity of these films. Measurements before and after exposure to high vacuum were done to address the possibility of residual or trapped solvent in the films over the curing time, and sample integrity under positron beam conditions. Data were the same in both conditions, indicating the aged samples were robust and experimental data not affected by residual solvent.

In contrast, the Deft-98 aqueous-base primer films exhibit a significant difference in their intensities ($I_3$), dependent on the orientation of the face (refer to Fig. 1 and Table 1). In all samples, 7-day cure, 21-day cure, and aged Deft-98, the $I_3$ value of the sample in the back-to-back orientation exhibited a lower value, and the associated free fractional volume decreased in value. In the average lifetime measurement, a ‘homogeneous’ material should exhibit the same lifetime, intensities, etc. regardless of orientation. In comparing the lifetime measurements here, the observed intensity difference is taken to mean that some heterogeneity exists in the internal structure of the Deft-98 primer films vs. Deft-84.

In addition, the average o-Ps lifetime ($\tau_3$), and calculated pore size ($R$) decreased over the curing time of 7 and 21 day, to aged samples. Figure 2 illustrates the lifetime, pore size, and radius distribution differences for the Deft-98 primer films analyzed in this project. At 7 days the pore radius is approximately 3.0 Å and decreases to about 2.7 Å in the fully aged film (also compare lifetime data, Table 1). For comparison, the aged Deft-84 organic-base primer has a pore radius about 3.0 Å (data not shown, but compare o-Ps lifetime).

3.2. Monoenergetic DBES and PALS evaluation of primer films.

Depth profiling and lifetime measurements using the monoenergetic positron beam at UMKC corroborated the proposal of structural differences in the two faces of the Deft-98 primer film, as well as differences between the two types of primer films. The film layer differences may arise from the emulsion-to-film formation process, which is a key difference between the aqueous-based primers compared to organic-based systems.
**Table 1.** Ortho-positronium pickoff annihilation lifetimes in primer films. Fresh Deft-98 primer films (aqueous-base) exhibit significant heterogeneity in intensity when comparing the back and front faces of the film, and exhibit a decrease in lifetime over time.

| Sample       | Face | \( \tau_3 \) (ps) | \( I_3 \) (%) | \( \Delta I_3 \) | FWHM (ps) |
|--------------|------|-------------------|--------------|----------------|------------|
| Deft-84 aged | Front| 2190              | 6.5          | 0.1            | 253        |
| Deft-84 aged | Back | 2210              | 5.7          | 0.1            | 140        |
| Deft-98 7 day| Front| 2130              | 9.9          | 0.1            | 201        |
| Deft-98 7 day| Back | 2180              | 5.0          | 0.1            | 144        |
| Deft-98 21 day| Front| 2050              | 9.6          | 0.1            | 243        |
| Deft-98 21 day| Back | 2060              | 6.5          | 0.1            | 209        |
| Deft-98 aged | Front| 1900              | 7.8          | 0.1            | 221        |
| Deft-98 aged | Back | 1960              | 5.6          | 0.1            | 201        |

**Figure 2.** Mean lifetime, lifetime distribution, and approximate radius for front and back faces Deft-98 aqueous-base primer films over time. The arrow (\( \leftarrow \)) indicates increased age of film.

The films’ depth profiles are quite different comparing the front faces of the organic- or aqueous-based films (Figs. 3 & 4), or comparing the front and back faces of the Deft-98 film (Fig. 4). However, these differences may not have directly influenced the water transport phenomena previously reported.

The lifetime of \( \sigma \)-Ps can be more correctly expressed as a distribution, and the correlation to hole radius (using a spherical approximation) can be expressed as a the free-volume probability-density function, PDF (sample, Fig. 5) [12]. The front faces of all the films, using lifetime measurements at varied positron implantation energies, demonstrate a decrease in the pore radius, roughly starting at a similar radius (3.7 Å) near the surface and having a bulk radius near 2.8 Å. For the facing sides the hole radius distribution is broader for Deft-98 at the deeper positron implantation energy (data not shown).

The front face of the Deft-98 sample exhibits a radius near the surface slightly smaller than that observed in the back faces (refer to \( \tau_3 \) in Table 1 and estimated radius in Figure 2), and the distribution stays somewhat narrower at greater depth. This narrower distribution may be reflecting the thicker second layer in the front faces of the aqueous-base films, i.e. fewer inorganic particles leads to smaller void distribution. Further, at the largest implantation energy, the radius and distribution are similar between the front and back faces, suggesting that at the associated depth, the environment is now similar (e.g. a similar ‘bulk’ heterogeneous phase) when approached from the differing analytical directions.
In general, it appeared that the aqueous-based film exhibited broader void volume distributions than the organic-base primer film. An example of this is illustrated in Fig. 5, where the 7 and 21 day cured samples of the aqueous-base film are compared. The pore sizes in the Deft-98 may be trending to slightly smaller sizes, and in this and other comparisons the distribution of voids was characteristically broader.

Figure 3. The S parameter, derived from Doppler-broadening energy spectroscopy, versus positron incident energy (or depth) in the front (left) and back (right) faces of the Deft-84 organic-base film. The interface layers are characteristically similar in nature.

Figure 4. The S parameter, derived from Doppler-broadening energy spectroscopy, versus positron incident energy (or depth) in the front (left) and back (right) faces of the Deft-98 aqueous-base film. The S parameter fit to 2-layer models indicate a 500-600 nm layer on the front face compared to a <200 nm interface layer on the back (from VEPFIT [18]).

4. Conclusion
Positronium lifetime measurements of two different primer films indicated structural inhomogeneity in the aged, aqueous-based primer, as well as a smaller void radius in the film compared to the aged, organic-based primer film. Comparison of lifetime data at seven day curing time to longer curing times suggests that the film may still be undergoing structural development at the 7 day point. This observation may explain the differential curing and in-plane water transport phenomena observed previously [2]. Through-plane water transport phenomena may be impacted by the presence of the relatively thicker secondary layer of the front face of the aqueous-base primer film; this due to less pore interconnectivity from the lower distribution of inorganic particles in this part of the layer structure.
The depth profile of the aqueous-based primer film, observed via DBES, confirmed the structural differences in the faces of this film, and indicated a larger layer between the surface and bulk of the sample. Lifetime data indicate generally broader and changing void distributions through the aqueous film and curing process. The PAS and water transport results taken together point to the different curing and internal structural development and final forms of the two types of primer coating systems.

**Figure 5.** Free-volume radius distributions (PDF = probability density function, [12]) as a function of positron implantation energy (keV) for front faces of Deft-98 (7-day, left) and (21-day, right) samples.

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