

# Positron studies of polymeric coatings

by

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## Positron studies of polymeric coatings

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### Abstract

In complicated coating systems, positrons have shown sensitivity in detecting the early stage of deterioration due to weathering, specially, in probing a specific location or depth of coatings from the surface through interfaces and the bulk. Existing extensive experimental positron data show that positron annihilation signals respond quantitatively to the deterioration process due to weathering. Now it is possible to detect the very early stage of coating deterioration at the atomic and molecular scale by using positrons, typically in days as compared to years by conventional methods. This paper summarizes recent positron studies in polymeric coatings. Correlations between positron data and a variety of chemical, physical and engineering data from ESR, AFM, cross-link density, gloss, and cyclic loading are presented. © 2003 Elsevier Science Ltd. All rights reserved.

**Keywords:** Coatings; Weathering; Degradation; Polymers; Slow positrons

### 1. Introduction

The development of monoenergetic positron beams in recent years has enabled studies of surface properties of materials, in particular studies of atomic-scale defects at the surface and near-surface regions. Variable energy positron beams have been extensively used to study metal and semiconductor surfaces (Schultz and Lynn, 1988; Coleman, 2000; Krause-Rehberg and Leipner, 1999). In the case of polymers, these beams allow the determination of local free-volume properties of the polymers as a function of the depth from the surface (Jean et al., 1994, 1997; Xie et al., 1995; Gidley et al., 1995, 1997; Jean, 1995; Kobayashi et al., 1995; Cao et al., 1998a).

A polymeric coating is a multi-layer, multi-component, and multi-functional system. It contains a compo-

site of polymer (typically 80% mass fraction) and pigments (typically 20% mass fraction, such as TiO<sub>2</sub>). In such heterogeneous and complicated chemical systems, scientific curiosity has focused on applications of slow positrons to both fundamental and applied research in recent years. The early research (Szeles et al., 1988; Andreas et al., 1994; MacQueen and Granata, 1996) used positrons emitted from <sup>22</sup>Na radioisotope, which penetrates coatings to a depth of about 100 μm. The information is an integrated bulk property. Recently, the use of slow positrons has opened a new area of research. The slow positrons have been used to probe the surface, interfaces, multilayers, and bulk properties of coating systems (Hulett et al., 1995; Cao et al., 1998b, 1999a, b, 2000; Zhang et al., 2000, 2001a, b; Wu et al., 2001; Galindo et al., 2001; Weng et al., 2001; Jean et al., 2002; Chen et al., 2002; Mallon et al., 2002). It is fascinating in nature that slow positrons are capable of specifically probing the change in local free-volume properties due to environmental factors that control the applicability of coatings for protecting structural materials.

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Two main types of positron experiments have been made in polymers using a positron beam, namely, Doppler broadening of energy spectra (DBES) and positron annihilation lifetime (PAL) measurements. PAL measurements generally provide more quantitative information (such as free-volume size and distribution) than DBES studies, but in mono-energetic positron beams PAL is more complicated than DBES measurements due to the challenge of detecting the start signal for the positron lifetime. In DBES studies the momentum distribution around the 511 keV energy peak is monitored. A DBES spectrum is characterized by the  $S$  parameter, which is defined as the ratio of integrated counts in the central part of the peak to the total counts after the background is properly subtracted. Although  $o$ -Ps (*ortho*-positronium, a triplet state) has a longer lifetime in polymers than  $p$ -Ps (*para*-positronium, a singlet state), neither its three-photon nor two-photon pick-off annihilation contribute much to the  $S$  parameter of DBES spectra. Therefore, the  $p$ -Ps part of Ps annihilation contributes to the  $S$  parameter in DBES, while the  $o$ -Ps part of annihilation contributes to the long lifetime components, which are used to measure free-volume size, distribution and content in PAL.

In PAL, one uses the well-established relationship between  $o$ -Ps pick-off lifetime ( $\tau_3$  in a few ns) and spherical hole radius  $R$  (in a few Å) (Jean, 1990). Similarly, free-volume quantities and distributions could be estimated from the physical parameters in PAL data (Jean, 1995). For DBES data, three main factors contribute to the  $S$  parameter in polymers: (1) free-volume content, (2) free-volume size, and (3) chemical composition. First, a larger free-volume content contributes to a larger  $S$  value. DBES measures radiation near 511 keV where a major contribution comes from  $p$ -Ps. This  $p$ -Ps contribution is only  $\frac{1}{3}$  the  $o$ -Ps intensity of that in  $I_3$  of PAL data. Second, when  $p$ -Ps is localized in a defect with a dimension  $\Delta x$ , the momentum  $\Delta p$  has a dispersion according to the Heisenberg uncertainty principle  $\Delta x \Delta p \geq h/4\pi$ . The  $S$  parameter from DBES spectra is a direct measure of the quantity of momentum dispersion. In a larger size hole where Ps is localized, there will be a larger  $S$  parameter due to smaller momentum uncertainty. Therefore, in a system with many defects or voids, such as polymers, the  $S$  parameter is a qualitative measure of the defect size and defect concentration. The value of the  $S$  parameter also depends on the momentum of the valence electrons, which annihilate with the positrons. The value of the  $S$  parameter, therefore, may differ from polymer to polymer. Third, the  $S$  parameter depends on the electron momentum of the elements. As the atomic number of the element increases, the electron momentum increases, and thus the  $S$  parameter decreases. Fortunately, in chemicals of the same composition, the elemental effect on  $S$  could be small, and  $S$  data reflect mainly free-

volume properties in polymers. On the other hand, the  $S$  parameter is a useful parameter for detecting different chemical compositions in a multi-layer coating when its elemental composition changes. In this paper, both PAL and DBES results in polymeric coatings will be presented and discussed.

## 2. Depth profiles in polymeric coatings

When a positron with a well-defined energy is injected from a vacuum into a polymeric coating, it is either reflected back to the surface or it penetrates into the coating. The fraction of positrons that enter the coating increases rapidly as a function of the positron energy. As the positrons enter the coating, inelastic collisions between the positron and molecules slow down the positrons by ionization, excitation and phonon processes. The implantation-stopping profile  $P(z, E)$  of the positrons varies as a function of depth as (Schultz and Lynn, 1988) follows:

$$p(z, E) = -d[\exp - (z/z_0)^2]/dz, \quad (1)$$

where  $z_0$  is related to the mean implantation depth  $Z_0$  through the relation

$$z_0 = 2Z_0/\sqrt{\pi}. \quad (2)$$

$Z_0$  depends on the incident energy as

$$Z_0(E) = (400/\rho)E^{1.6}, \quad (3)$$

where  $Z_0$  is expressed in Å and  $\rho$  is the density in  $\text{g}/\text{cm}^3$ . A typical polymeric coating has a density of about  $1.5 \text{ g}/\text{cm}^3$ . Thus, with a typical university-base beam with an energy of 30 keV, one can easily probe the depth profile from the surface to a depth of about  $10 \mu\text{m}$ . The depth resolution is about 10% of the depth. As the positron enters deeper to the bulk, the depth resolution decreases. The best depth resolution is near the surface of coatings.

Fig. 1 shows an  $S$  parameter and  $o$ -Ps intensity ( $I_3$ ) vs. energy curve for a typical polyurethane (PU) and a polyurethane topcoat paint (PTG) containing a  $\text{TiO}_2$  pigment (Cao et al., 1999b). A distinct difference in the depth profile is observed. In both PU and PTG samples, there is an initial increase in the  $S$  parameter to a maximum value. In a coating containing pigments, there is a decrease in the  $S$  parameter at a depth greater than about 10 nm. This decrease is attributed to the effect of the  $\text{TiO}_2$  pigment, which contains electrons with high momentum and is also indicative of the fact that the coating contains a thin layer of pure polymers near the surface (Cao et al., 1998b). The  $S$  value for  $\text{TiO}_2$  powders has been measured to be 0.400 in the same slow-positron beam. The dashed lines in the figure indicate the location of the layer boundaries for the paint sample determined using the VEPFIT program (Van Veen et al., 1990). From the depth data, it has been

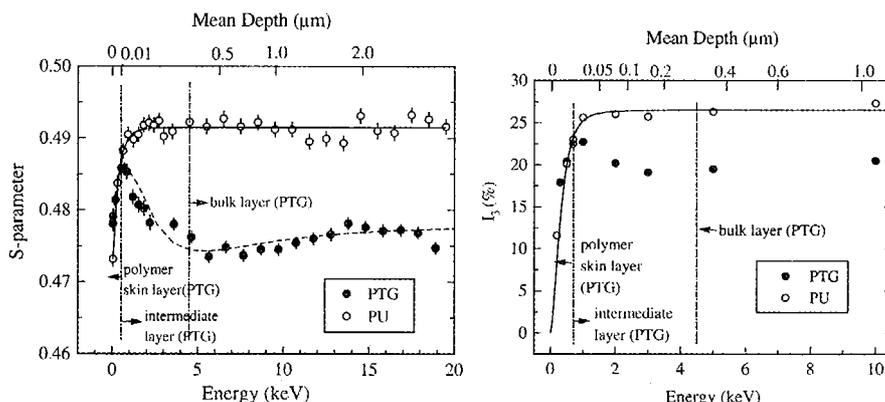


Fig. 1.  $S$  parameter (left) and  $o$ -Ps intensity (Cao et al., 1998b) as a function of positron incident energy for PU and a polyurethane topcoat containing  $\text{TiO}_2$  pigments (PTG).

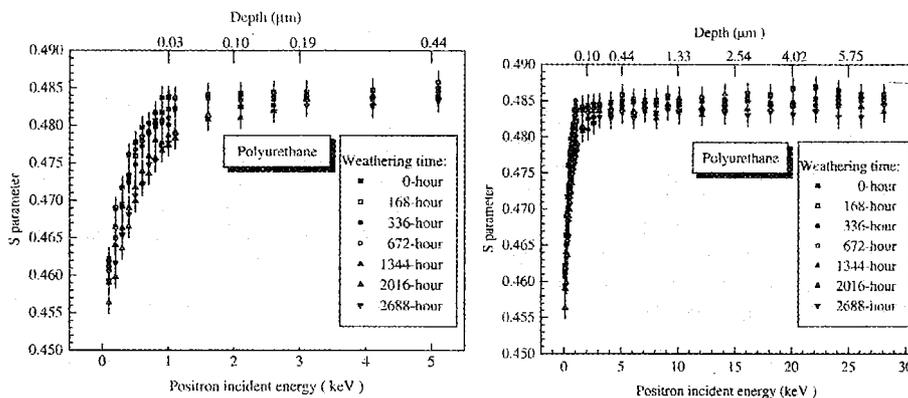


Fig. 2.  $S$  parameter vs. energy and depth in a PU coating at different periods of natural weathering (Cao et al., 1999b).

concluded that in coating systems containing  $\text{TiO}_2$ , (1) there exists approximately 10 nm of polymer skin from the surface of the paint, (2) inside the polymer skin there exists an intermediate transition layer (approximately 0.1–0.5 μm) where  $\text{TiO}_2$  starts to disperse with the polymer and other additives, and (3) inside the transition layer there exists the bulk layer of paint. It should be noted that the error bar on each data point in all figures given in this paper denotes one standard deviation.

### 3. Exposure to UV and degradation of coatings

On exposure to various weathering and aging conditions, a significant decrease in the  $S$  parameter has been observed. Slow-positron beam techniques are very successful in monitoring these changes in the very early stages of degradation of polymer coatings caused by accelerated weathering (Cao et al., 1998b, 1999a, b) as well as under natural weathering conditions (Jean et al.,

2002; Mallon et al., 2002). The great value of the technique has been the depth-profiling ability, which allows for the determination of the kinetic data of the degradation process as a function of the depth from the surface.

Fig. 2 shows the decrease in the  $S$  parameter as a function of exposure time due to natural weathering for a PU coating (no pigment) (Cao et al., 1998b). Fig. 3 shows the magnitude of the change in the  $S$  parameters as a function of exposure time as follows:

$$-\Delta S = S_t - S_0, \quad (4)$$

where  $S_t$  is the  $S$  parameter at a certain depth after exposure time  $t$ , and  $S_0$  is the  $S$  parameter at that depth of the unexposed sample. These figures clearly illustrate that there is a decrease in the  $S$  parameter as a function of exposure time.

It has been suggested that the decrease in the  $S$  parameter on exposure time is a result of decreases in the defect (free volume) size and concentration due to irradiation (Cao et al., 1999a). This indicates a change in the cross-linking density of the samples as a result of

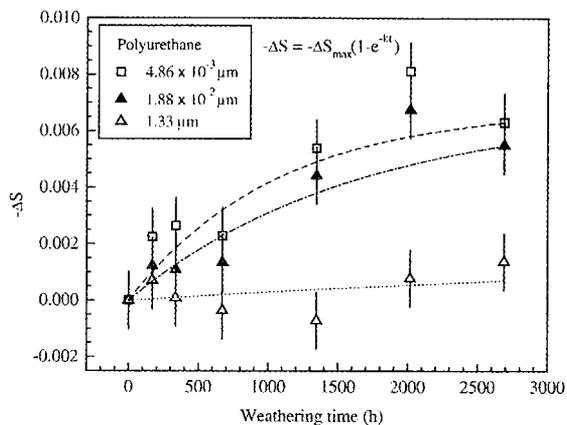


Fig. 3.  $-\Delta S$  vs. weathering time at different depths from the surface (Cao et al., 1998b).  $-\Delta S$  is calculated according to Eq. (4) from data shown in Fig. 2. Lines are fitted to Eq. (5).

photodegradation. It has been demonstrated that there is a direct relationship between the decrease in the  $S$  parameter (loss of free volume) and an increase in the cross-linking density due to degradation for PU coatings (Zhang et al., 2001a, b). We can postulate that the  $-\Delta S$  is a measure of the product concentration of the degradation process (which appears reasonable in light of the relationship between  $-\Delta S$  and cross-linking density). The  $-\Delta S$  vs. time plots can be fitted to an exponential function (Cao et al., 1998b, 1999a, b) for polymer coatings:

$$-\Delta S = -\Delta S_{\max}(1 - e^{-kt}), \quad (5)$$

where  $t$  is the time of exposure and  $k$  is a rate constant. A good fit of this exponential function indicates a first-order kinetics of the degradation process, at least near the surface. The half-life of the degradation can also be determined from the first-order kinetics using the relationship (Wu et al., 2001)

$$t_{1/2} = \ln \frac{2}{k}. \quad (6)$$

This  $t_{1/2}$  value is a characteristic parameter representing the durability of the coating with respect to weathering or photodegradation (Wu et al., 2001).

It can also be seen from Figs. 2 and 3 that effects of weathering are more pronounced near the surface and decrease progressively into the bulk. This is not surprising and the decrease in the magnitude of the change of the  $S$  parameter as a function of depth can be explained by the attenuation of the light intensity with increasing depth from the surface. Fig. 4 shows a plot of the  $-\Delta S$  vs. depth for two exposure times of the samples shown in Fig. 2. The variation of  $-\Delta S$  vs. depth ( $d$ ) can be expressed by an exponential decay function according to the following equation for a coating without

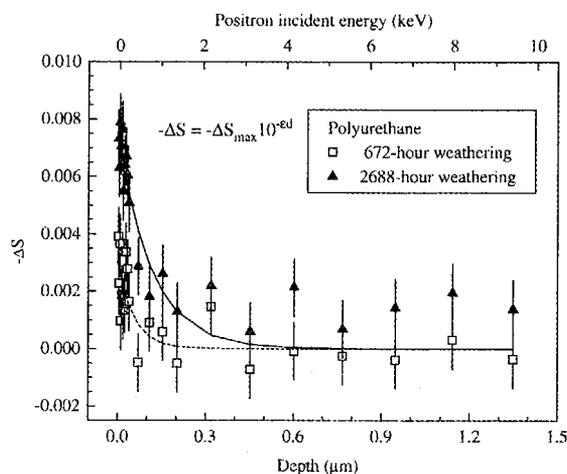


Fig. 4.  $-\Delta S$  vs. positron incident energy and depth for PU coating exposed to natural weathering for 672 and 2688 h (Mallon et al., 2002). The line in the figure is fitted according to Eq. (7).

pigments:

$$-\Delta S = -\Delta S_0 \times 10^{-\epsilon d}, \quad (7)$$

where  $-\Delta S_0$  is the fitted  $-\Delta S$  at  $d = 0$  and  $\epsilon$  represents a parameter with a property similar to the extinction coefficient for UV absorption.

#### 4. Durability of commercial coatings and paints<sup>1</sup>

In commercial coatings containing  $\text{TiO}_2$  the  $-\Delta S$  vs. depth curves are best fitted with a two-exponential decay function (Wu et al., 2001; Zhang et al., 2001a, b). The three polymeric coatings shown in figures are produced under the commercial names of Carboline 133HB (a PU-based paint), Macro Epoxy 646 (an epoxy-based paint) and Devflex 4206 (an acrylic-based paint). All these samples contain  $\text{TiO}_2$  as a pigment. The lines in the Fig. 5 are fit according to the equation (Wu et al., 2001; Zhang et al., 2001a, b) for coatings with pigments:

$$-\Delta S = -\Delta S_1 \times 10^{-\epsilon_1 d} + (-\Delta S_2) \times 10^{-\epsilon_2 d}, \quad (8)$$

where  $d$  is the depth and  $\epsilon_1$  and  $\epsilon_2$  are the first and second extinction coefficients. The fact that a two-exponential decay function best fits the data for the commercial coatings is indicative of the fact that the coatings consist of a multi-layer with a polymer skin, followed by a transition layer and the bulk.

<sup>1</sup>Certain commercial product or equipment is described in this paper in order to specify adequately the experimental procedure. In no case such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

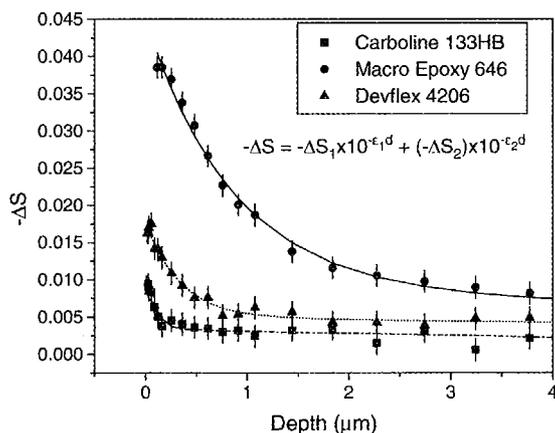


Fig. 5.  $-\Delta S$  vs. positron implantation depth for commercial coatings after 2688 h of natural weathering. Lines in the figure are fitted with Eq. (8).

Positron data of  $S$  parameters have been used to characterize the durability of a variety of commercial coatings and paints (Mallon et al., 2002). A larger  $-\Delta S$  indicates a poorer durability against weathering. Among those three commercial samples, the order of durability against weathering is Carboline 133HS (polyurethane base) > Devflex 4206 (acrylate base) > Macro Epoxy 646 (epoxy base), which are consistent with their coating performance.

## 5. Correlation with other properties

### 5.1. ESR

The changes in the  $S$  parameter on exposure to weathering have been correlated to many other chemical and physical changes in the coatings. It has been shown, for example, that there is a direct correlation between the  $-\Delta S$  value and radical intensity measured by electron spin resonance (ESR) in the coating (Cao et al., 1999b). Fig. 6 shows the correlation between the intensity of the ESR signal and the change in the  $S$  parameter for both a catalyzed and a noncatalyzed PU coating due to ex situ UV irradiation. This figure illustrates the role of free radicals in the microstructural changes that take place in the coatings. This correlation has been used to investigate the photodegradation mechanism of polymeric coatings (Cao et al., 1998b, 1999a, b).

### 5.2. Cross-link density

The change of cross-link density after UV irradiation indicates that some new bonds are formed between the

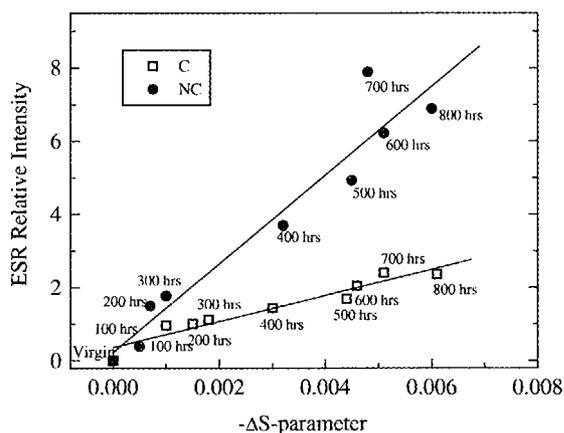
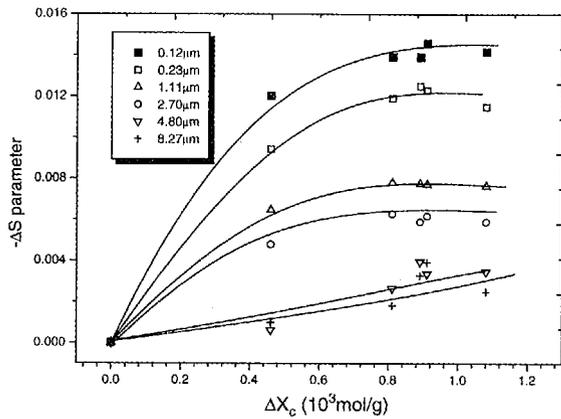


Fig. 6. Correlation between intensity of ESR signal and decrease in the  $S$  parameter of PAS data due to ex situ UV irradiation for catalyzed (C) and non-catalyzed (NC) PU (Cao et al., 1999a). The  $-\Delta S$  values are the average of the bulk data.

polymer chains. The formation of new bonds and the increase in cross-link density will decrease the free volume in the polymer. The  $\Delta S$  parameter describes the change of free volume in polymeric material. Fig. 7 expresses the correlation of  $-\Delta S$  (loss of free volume) and  $\Delta X_c$  (increase in cross-link density) at different depths of PU (Zhang et al., 2001a, b).  $\Delta X_c$  is the overall change of cross-link density for the whole sample by the solvent swelling method.  $\Delta S$  on the surface and near the surface increases significantly, while  $\Delta S$  in the bulk shows little change. This means that cross-link formation and the resultant collapse in free volume at the surface contributes most to the cross-link density changes in the early stages of exposure. Cross-link density ( $X_c$ ) of the coating material PU is found to increase after UV irradiation. This indicates the collapse of free volume during degradation. The  $S$  parameter from DBES and  $I_3$  from PAL describes the depth profile of free volume from the surface to the bulk. There is a correlation between  $\Delta X_c$  and  $\Delta S$  at different depths and at the integrated overall depth, as shown in Fig. 7.

### 5.3. Gloss

One physical property regarded by the coating industry as important is gloss, which is a measure of surface roughness. Since PAS has a capability to measure atomic-scale defects from the surface to the bulk, we conducted parallel experiments on glossiness and PAS measurements in a model PU coating. Fig. 8 shows  $S$  defect parameter vs. positron incident energy for PU under different durations of UVB (313 nm) irradiation (Wu et al., 2001).



Correlation between  $\Delta X_c$  and average  $-\Delta S$  parameter

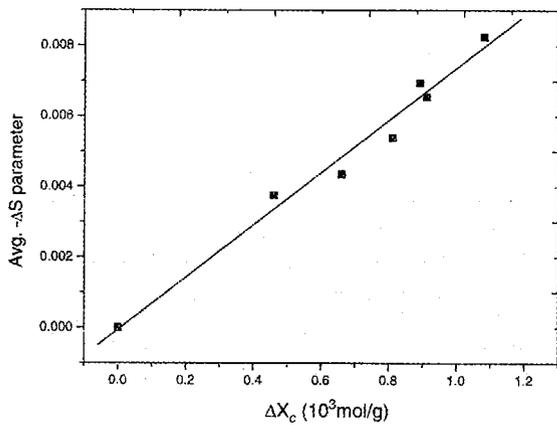


Fig. 7. Correlation between the loss of free volume ( $-\Delta S$ ) and increase of cross-link density. The top is for all depths and the bottom figure is an average of all depths as Xe-lamp light penetrates through the PU samples (Zhang et al., 2001a, b).

**$\Delta G$  (glossiness) vs  $\Delta S$  parameter**  
Polyurethane under UVB-313 irradiation in air

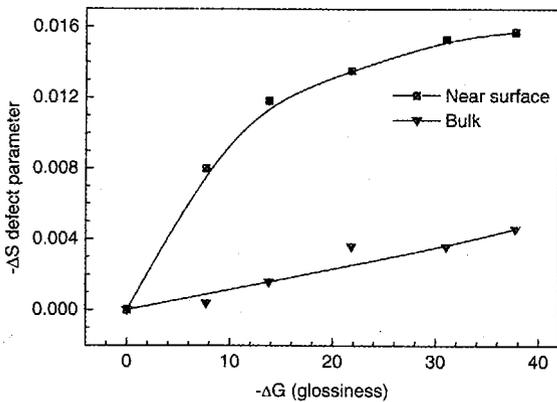


Fig. 8. Correlation between the loss of free volume and loss of gloss in a PU sample exposed to UVB (313 nm) irradiation (Wu et al., 2001).

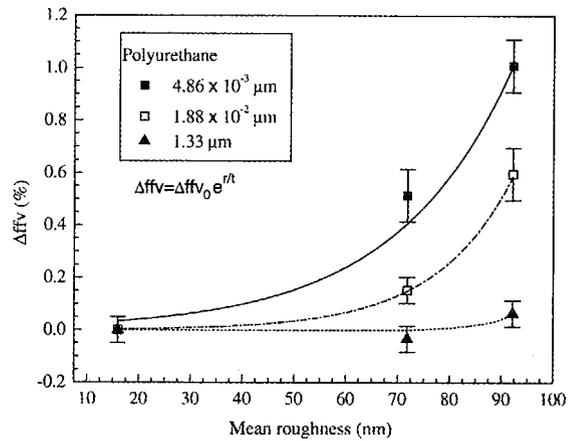


Fig. 9. Correlations between the loss of ffv from PAL vs. mean roughness measured by AFM (Wu et al., 2001).

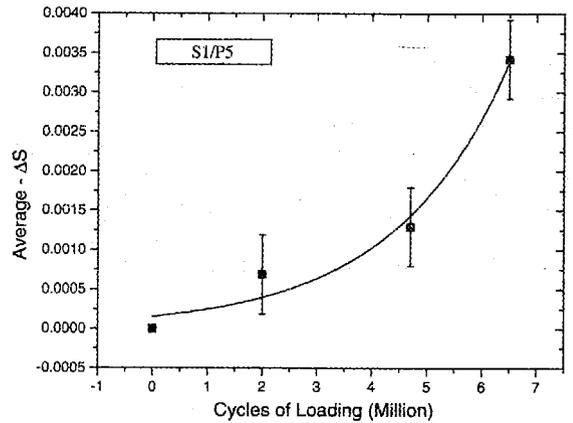


Fig. 10. A direct correlation between the loss of free volume ( $-\Delta S$ ) at the molecular level and cycle of loading in a sulfonate coating (Chen et al., 2002).

5.4. Surface roughness

Recently, we performed a direct comparison of surface morphology from AFM in a PU sample exposed to Florida natural weathering and free-volume fraction (ffv) at different depths. Fig. 9 shows direct correlations between the loss of free volume and increase in roughness (Wu et al., 2001).

5.5. Mechanical loading

The mechanical durability of coatings has been tested by applying the cyclic loading until the coating is failed visibly. A parallel experiment of positron annihilation studies on the same samples has been performed (Chen et al., 2002). A correlation between the loss of free volume ( $-\Delta S$ ) and the loading cycle has been observed

in a commercial coating, as shown in Fig. 10. It is interesting to observe a direct link between an engineering parameter and a molecular physical parameter obtained by the positron annihilation method.

## 6. Conclusion

Positron annihilation in polymeric coatings provides new information about (1) early detection of deterioration on the order of a few days of natural weathering, (2) depth profile information from the surface to the bulk, and (3) degradation information at the molecular level. Good correlations between the microscale positron data and a variety of macroscopic data are observed. The existing data show great promise to develop positron annihilation as a sensitive new tool for the detection of coating degradation and improving coating durability. Real-world applications of PAS as a field tool require additional systematic studies and engineering collaboration in the future.

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