ASSAY OF WEATHERING EFFECTS ON PROTECTIVE POLYMER
COATINGS USING POSITRON ANNIHILATION SPECTROSCOPY

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ABSTRACT

Polymer coatings, both with and without pigments, have been subjected to solar radiation and water spray weathering. The degrees of penetration of the weathering effects have been measured by injecting positrons of varying energy, i.e. to variable depths, into the films and observing the Doppler broadening of the annihilation radiation. The method is capable of detecting changes due to weathering effects at very early stages, long before visual examination reveals degradation. As little as one week of exposure caused measurable changes in the polymer structure, which were reflected in the Doppler broadening. Given further development, positron spectroscopy could possibly become a useful complement to the other methods of determining weatherabilities of protective polymer coatings.

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Introduction

Manufacturers of paints are obligated to produce protective coatings with as high resistivity as possible to degradation by weathering. Determining the weathering resistance of paints is very time consuming. Exposures of one year or more to weathering are often necessary to assess durabilities. It is desirable for spectroscopic techniques to be developed that will detect the early onset of degradation. Such methods will decrease testing time and enable faster developments of polymer coatings with high protective capabilities.

Positron spectroscopy is known to be a non-destructive technique with the ability to detect structural and chemical changes in polymers. This has led to the studies reported in this paper, in which the Doppler broadening measurements of positron annihilation spectra have been recorded as functions of depth in polymer paint films. Spectra for weathered films are significantly different from those of unweathered films.

Positron Annihilation Processes in Polymers

The two most commonly used positron spectroscopy methods for materials characterization are positron annihilation lifetime spectroscopy (PALS) and Doppler broadening of annihilation radiation (DBAR). The lifetime method has been used extensively

by many workers to study polymers. Jean [¹] has recently discussed the method in general, and Jean and Deng [²] have demonstrated the ability to quantify mean free volume size and free volume size distributions. In this work a slow positron beam, having controllable energy, was used in order to vary the penetration depths of positrons into the polymer coatings and determine the depths to which weathering penetrated. The DBAR method was used to monitor the annihilation characteristics of the implanted positrons.

Some of the positrons injected into polymers form positronium atoms, with the spins of the electrons parallel to those of the positrons, which are captured in the free volume interstices. In this state the positrons are protected against annihilations for longer lengths of time, but eventually they are picked off by other electrons having opposite spins, resulting in immediate annihilations. Jean³ has demonstrated, for the case of epoxy polymers, that the net momenta of the positron-electron pairs involved in pickoff annihilation events tends to be low. Outside the free volume interstices the positrons annihilate as unbound particles with valence electrons and with core electrons, which have high momentum. Annihilation with high momentum electrons gives rise to an appreciable amount of Doppler broadening of the 511 keV annihilation photopeak. Doppler broadening of radiation from positronium annihilation events is smaller.

Under well-defined circumstances, broadening of the 511 keV peaks can be ascribed to reductions in free volume contents of polymers. Such is the case with the work of Jean and Deng (1,2,3), where free volume content was altered by physical processes (temperature and pressure changes). For this work, however, changes in Doppler broadening may be due to more complex factors. Studies such as that of Bauer et al. [4], show that weather-induced photooxidation processes can produce hydroperoxides, carbonyl groups and free radicals in polymer films. This sort of change in the chemistry of polymers can significantly alter the probability of positronium formation and decay. For the work reported in this paper, chemical as well as physical changes have occurred in the polymer films.

Preparation and Weathering of Specimens

Water-based paints having two types of polymer binder, styrene-acrylic and all-acrylic, have been studied. They were applied as 25 - 40 micrometer films to aluminum substrates. Panels containing binder only, with no TiO_2 pigment, and panels containing binder plus 40% pigment volume content (PVC) were prepared. The panels of water-based specimens were oven dried at 165°C for 10 minutes. The acrylic and styrene-acrylic binders contained melamine crosslinking agents. In addition, one organic solvent-based (mineral spirits) paint, having an alkyd polymer binder plus 40% PVC TiO_2 , has been studied. It was applied to

aluminum substrates and dried at room temperature for 5 days.

The styrene-acrylic and all-acrylic paint panels were weathered at the EMMAQUA facility, located near Phoenix, Arizona. This device subjected the specimens to concentrated sunlight reflected from an array of mirrors. During daylight hour exposures the panels were periodically sprayed with water at one-hour intervals. During the night hours they were sprayed at 3-hour intervals. The panels covered with water-based paints were given 15 day weathering treatments at the EMMAQUA facility. Radiation fluence was 2282 MJ/m² total, 48 MJ/m² ultraviolet. The panel covered with the solvent-based alkyd paint was exposed continuously for 5 days to an intense xenon lamp with 18 minute water spraying at 102 minute intervals.

DBAR Measurements of Paint Films; Data Processing

Doppler broadening of positron annihilation radiation (DBAR) measurements were made at Brookhaven National Laboratory, using a variable-energy positron beam generated by fast positrons from a ²²Na source, moderated with an annealed tungsten film. Injection energies as high as 70 keV could be imposed and they were stepped in 250 eV increments. One million counts were collected in the 511 keV peak for each positron injection energy. The degree of Doppler broadening of the annihilation photopeaks was quantified by the S parameter (line shape parameter), which is

the ratio of the area of the mid-portion of the peak to the total peak area. Depths of penetration by the positrons in the paint films were estimated using the calculations of Ashley [⁵]. For the films containing pigment, penetration depths were estimated by considering the greater stopping power of titanium. Depth estimates are only approximate. More accurate calculations of penetration depths using Monte Carlo methods are needed for polymers.

Results and Discussion

With the unaided eye, no differences could be discerned between the paint specimens that had been weathered and those that had not. For all specimens studied, however, S parameter vs positron injection energy (S-E) curves show that weathering causes significant structural changes.

Figure 1 shows S-E curves for films of all-acrylic binder. The calculated depth of penetration of the positrons is plotted along the upper abscissa. These specimens had no TiO₂ pigments, being completely transparent. It is seen that, for all positron energies, the S parameters for the 15 days weathered film are lower than those of the non-weathered specimen. Figure 2 compares S-E curves for films of styrene-acrylic binders (no pigment). For these coatings also, it is seen that weathering lowers the S parameter values.

For both the all-acrylic and the styrene-acrylic binders, Figures 1-2, the S parameters increase with depth into the film. As discussed above, larger S parameters may be caused by higher free volume content of polymers, as seen by positronium atoms.

Free volume increase with depth into the films is a possible explanation for the shape of the S-E curves in Figures 1-2. It is also possible, however, that the lower S parameters near the surface are artifacts, due to the diffusion of injected positrons back to the surface, where they annihilate with higher-momentum electrons.

Figure 3 compares S-E curves for styrene-acrylic films that contained 40% TiO_2 pigment. It is seen that the weathering has caused the S parameters to decrease for this specimen also. Note that for low energies of positron injection, less than 500 eV, the S parameters of Figures 1 and 3 are about the same, but for injection energies above about 1 keV the S parameters in Figure 3 decrease sharply with depth. This suggests that the outermost surfaces of the films are rich in binder and depleted in TiO_2 pigment and that the S parameters are smaller at greater depths in the film because of increased concentrations of pigment. The greater degree of Doppler broadening may be partly due to the annihilation of positrons with the high-momentum outer core electrons present in the titanium atoms, but the explanation may be more interesting than this: Possibly the increased Doppler broadening is reflecting increases in electron momentum induced

by effects at the pigment-binder interfaces. The presence of the pigment does not appear to obscure the interpretation of the weathering effects. It can be concluded that weathering causes about the same degree of structural change on the outer surfaces of pigmented films as it does in transparent films. It appears, however, that pigmentation reduces the weather penetration into the film. Figure 3 indicates that the S parameters of both films begin to merge to the same value for depths greater than 10 micrometers, which is considerably more shallow than the penetration depths of the non-pigmented films.

This effect is more clearly seen in Figure 4, for the organic solvent based alkyd-binder film, containing 40% TiO_2 . For these measurements positron injection energies up to 60 keV were used. The differences in the S parameter curves for the weathered and non-weathered films are qualitatively similar to those of Figure 3. It is seen that the 5 days xenon lamp weathering decreases the S parameters for shallow depths into the film. Beyond a depth of about 20 micrometers, however, the S parameters are the same for both specimens, suggesting that weathering effects did not penetrate further.

The results of other workers in the field of polymer degradation should be strongly considered in the interpretation of the data presented in this paper. A possible explanation of the observed decreases in S parameters is that weathering caused a lowering

of the positronium production rate by reducing the free volume content of the polymer. However, the work of Bauer et al. [4] suggests that cross linking scissions can occur during weathering, which should cause increases in free volume rather than decreases. The production of hyperoxides, carbonyl groups, and free radicals are also reported. It is possible that these affect the electronic properties of the polymer to such an extent that, even though free volume increases occur, the formation of positronium becomes less probable. Further studies, using positron lifetime techniques, electron paramagnetic resonance, and other methods are needed to address this question.

Summary and Conclusions

Doppler broadening of positron annihilation spectra can be used to detect the early onset of weathering effects on the properties of protective polymer films. Positron spectroscopy techniques have the potential to contribute to the development of faster methods for predicting the durabilities of polymer coatings. Eventually, positron annihilation lifetime spectrometry, which supplies more detailed information than DBAR, will also be applied to the analysis of polymer films. It should be emphasized that positron techniques are non-destructive.

It has been demonstrated that the depths of penetration of weathering can be detected by positron spectroscopy methods. A

determination of the nature of the structural changes in the paints, e.g., whether free volume or chemical changes occur, has not been accomplished by these initial studies, but useful information on this aspect will be forthcoming in future work.

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Figure Captions

Figure 1. The effect of weathering on DBAR S-parameters of water-based acrylic paint binder films as functions of positron injection energy. Films were visually transparent, with no TiO_2 pigment.

Figure 2. The effect of weathering on DBAR S parameters of

water-based styrene-acrylic paint binder films as functions of positron injection energy. Films were visually transparent, with no TiO_2 pigment.

Figure 3. The effect of weathering on DBAR S parameters of water-based styrene-acrylic paint films, having 40% TiO_2 pigment, as functions of positron injection energy.

Figure 4. The effect of weathering on DBAR S-parameters of organic solvent based alkyd paint films as a function of positron injection energy. Films contained 40% pigment volume content TiO_2 .

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Figure 1

Figure 2

Figure 3

Figure 4