Degradation of Polymer Coating Systems Studied by Positron Annihilation Spectroscopy. 3. Wavelength Dependence of UV Irradiation Effect

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ABSTRACT: Photodegradation of a polyurethane coating induced by accelerated UV irradiation is studied using three different light sources: 340 nm UVA, 313 nm UVB, and Xe lamps. Doppler-broadened energy spectra (DBES) and positron annihilation lifetime (PAL) are measured as a function of incident positron energy (0−30 keV) and of irradiation time (0−800 h). The photodegradation of the coating is characterized in terms of subnanometer defect changes. Significant variations of S parameter, orthopositronium lifetime, intensity, and lifetime distribution are observed as a function of depth and of exposure time. These results indicate a decrease of free volume and holes at the atomic level during the degradation process. The UV irradiation at 313 nm shows a significant effect compared with that at 340 nm on the photodegradation: (1) the magnitude of S reduction increases a factor of 2 near the surface; (2) the photodegradation rate increases ∼25 times near the surface; (3) the irradiation effect attenuates with depth, and a larger extinction coefficient is observed with shorter wavelength UV irradiation. The observed effect by Xe light irradiation is the strongest among these three light sources. Enhanced degradation at shorter wavelengths is also indicated by increased free radical production, as observed by electron spin resonance spectroscopy.

Introduction

Degradation of polymeric coating materials due to environmental factors, such as moisture, light, oxygen, fluid, and salt, is the main source of reduced service lifetime for the coating systems. Much knowledge of coating degradation and failure can be obtained using accelerated testing. In our recent studies,[1,2] we used an innovative nondestructive technique, positron annihilation spectroscopy (PAS), to investigate the properties of subnanometer defects in polymeric coating systems during photodegradation processes induced by accelerated UV irradiation.

PAS is a special nanoprobe technique that has been developed to directly determine the local free-volume hole properties in polymeric materials.[3−9] Because of the relative small size of the positronium (Ps) probe (1.59 Å) and the small time scale of the probe lifetime (∼nanoseconds), PAS is particularly sensitive to small holes and free-volume defects in a size range of 1−20 Å and at a time of molecular motion from 10^{-10} s and longer. Physical properties of unoccupied spaces, such as free volume and holes, are thought to directly relate to photodegradation processes in polymers. For example, the photochemical process is affected by the fractional free volume which controls molecular relaxation and diffusion of small molecules (e.g., O_2, and small radicals such as $H^{\bullet}$ and $CH_3^{\bullet}$).[10] On the other hand, photodegradation can cause free-volume property changes in polymeric materials. The detection of molecular-level microstructural changes of free volumes and holes in the early stage of the degradation will provide an understanding of the origins, mechanisms, and progression of the photodegradation process, which eventually leads to macroscopic structural changes and loss of coating durability.

In our previous studies,[1,2] we used one of the positron annihilation techniques, Doppler-broadened energy spectra (DBES), to examine the defect profile (i.e., defect parameter S as a function of depth) near the surface of the polymeric coatings. Significant decreases in the S parameter were observed as a function of UV irradiation duration in a clear polyurethane coating system[2] and a polyurethane-based aircraft paint.[1] The decrease in the S parameter indicates loss of free volume induced by UV irradiation. Changes in physical defects have been further investigated by the formation of free radicals due to photochemical processes. A correlation between $-\Delta S$ by PAS and the free radical concentration by electron spin resonance (ESR) due to photodegradation has been observed.[2]

In this work, UV irradiation effects on polyurethane coatings are further investigated by using UV light sources with different wavelengths. Natural sunlight has a broad wavelength distribution ranging from 300 to 2500 nm. The ultraviolet region ($\lambda < 380$ nm), which only accounts for 5% of the total spectral radiation, is mainly responsible for the natural degradation of polymeric materials because of high-energy photons interacting with molecules and initiating photochemical process. The UV region is generally further classified into three components: UVA (320−400 nm), UVB (290−320 nm), and UVC (<290 nm). Due to ozone absorption

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in atmosphere, the UVC region becomes of negligible intensity when the sunlight reaches the earth. For the intermediate UVB range, despite ozone absorption, a substantial fraction of UVB radiation still reaches the earth's surface. The UVA region is little affected by the ozone absorption. Although the light intensity of the UVB region is much weaker than the UVA, its effect on the degradation of polymer coatings is significant because its higher photon energy dramatically enhances photochemical reactions. Characterization and comparison of degradation effects under different UV wavelength conditions will help improve our understanding of the degradation mechanism and provide valuable information for evaluating the applicability of accelerated weathering methods. In this paper, we report the results of irradiation effects in a commonly used polyurethane coating by using UVA, UVB, and xenon lamp light sources.

Experimental Section

The polyurethane (PU) used in this study was a two-component coating system, which was prepared by mixing commercially supplied raw materials, polyisocyanate (composed of hexamethylene diisocyanate units oligomerized via urea and biuret linkages, equivalent weight = 191) and polyester–polyol (composed of phthalic acid, adipic acid, and trimethylolpropane units, equivalent weight = 200), in an equivalent ratio 1.05:1. Additional polyisocyanate was applied in order to react with the polyurethane product to form allophanate linkages. The chemical structures of these raw materials can be found in our previous paper.[2] The density was determined to be 1.100×10^3 kg/m^3. The T_g was 68 °C as measured by a DSC (Polymer Labs, model 3) at a scanning rate of 10 °C/min. The UV–vis absorption spectrum of the polyurethane showed strong absorption in the UV region with wavelengths <300 nm. The polyurethane was immediately spin-coated onto aluminum plates and cured in the atmosphere for 48 h. The thickness of the coating was determined to be ~200 μm from profilometry.

Three types of artificial light sources were applied in the accelerated UV irradiation of the PU coating samples: QUV accelerated weathering chamber (from Q-panel Corp., Cleveland, OH) with UVA-340 fluorescent lamps, QUV chamber with UVB-313 fluorescent lamps, and xenon light source (4.5 W optical output, SLM Instrument, Inc., Urbana, IL). The spectra of sunlight in the UV region, UVA-340, UVB-313, and Xe light are plotted in Figure 1. The UVA-340 spectrum has its highest intensity at 340 nm with a full width at half-maximum (fwhm) of ~50 nm. The UVB-313 spectrum has its highest intensity at 313 nm with a fwhm of ~40 nm. Both lamps were set to a 0.85 W/(m^2 nm) peak irradiance, which, in the case of UVA-340, corresponds to the UV intensity of summer noon sunlight as shown in Figure 1. The UVA-340 lamp output is similar to the sunlight UV region spectrum. The UVB-313 lamp includes the shortest wavelengths found in sunlight at the earth's surface. The temperatures in the QUV chambers were automatically controlled at 45 and 50 °C for UVA-340 and UVB-313, respectively. Similar to sunlight, the xenon light has a broad spectrum. The emission output is continuous in the visible range and extends into the UV as well as having some strong lines in the near-infrared region. About 6% of the Xe lamp output is in the region 250–350 nm, with 2.5% in the region 250–300 nm and 3.5% in 300–350 nm. The irradiance of the xenon lamp in the effective UV region is about 10-fold greater than the total irradiance of the UVA-340/UVB-313 lamps.[2]

Positron annihilation lifetime (PAL) and Doppler-broadened energy spectra (DBES) techniques coupled with a slow beam were used to measure the PU coating samples. The PAL experiments were performed at the intense slow-positron facility in the Electrotechnical Laboratory (ETL) in Japan.[13] The lifetime resolution was 250 ps at a counting rate of 1000–1500 counts/s. Each PAL spectrum contains 1 million counts. The DBES experiments were performed at Brookhaven National Laboratory.[14] The energy resolution was 1.5 keV at 0.511 MeV (corresponding to the positron 2γ annihilation peak). The total count for each DBES spectrum is 0.5 million with the counting rate of 4000 counts/s. The obtained DBES data are characterized by the S parameter, as a measure of the momentum broadening. The S parameter is defined as the ratio of the central area (509.51–512.59 keV) to the total counts after the background is properly subtracted. The obtained PAL data were fitted into three lifetimes using the PATFIT[15] program. The longer lifetime components from backscattered positrons in a vacuum were neglected by limiting the fitting range to <10 ns.[9] Continuous lifetime distribution analysis was performed by using the MELT[16] program.

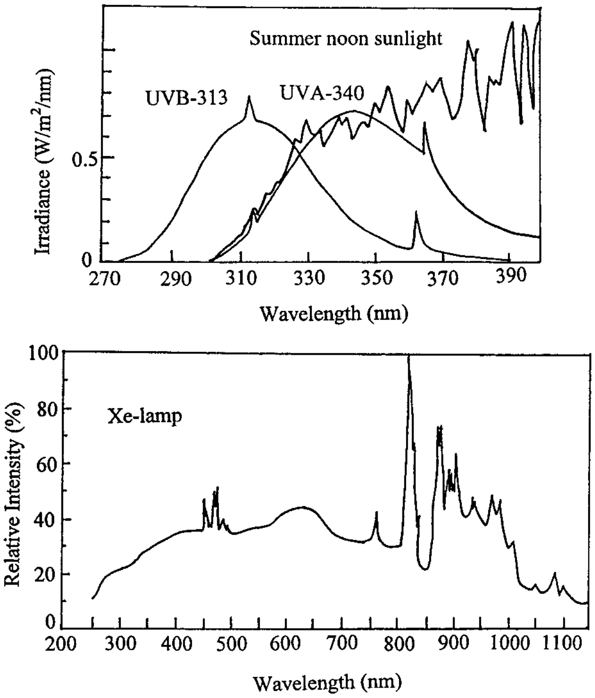

Figure 1. Emission spectra of UVA-340 and UVB-313 light sources compared with natural sunlight in the UV region (upper)[11] and Xe lamp (lower) output spectrum.[12]

ESR experiments were performed on the PU samples to detect the free radicals involved in the photochemical reactions. The spectra were recorded using a Bruker ER-200-D X-band ESR spectrometer. Spectral scans were generally 15 mT and were averaged from 3 to 10 scans at a scan rate of 0.30–0.75 mT/s. The modulation amplitude was typically 0.5 mT.

Results and Discussion

In our recent paper,[2] the DBES results from PU coating samples irradiated by UVA-340 and Xe light sources were reported. Both of the results showed a significant decrease in the S parameter near the surface of the coating with the increasing irradiation duration. The magnitude of the S parameter decrease was found to be a function of irradiation time and depth from the surface and was also strongly dependent on the light sources. Xe light appears to have much stronger effect than UVA-340 near the coating surface. Since Xe light has a much broader spectrum (250–1100 nm) than UVA-340 (300–400 nm) (Figure 1) and its intensity is 10-fold stronger than the UVA-340 lamp, both factors could contribute to the stronger effect observed in Xe-exposed samples. A comparison of the previous results with the current UVB-313 results will be discussed in terms of the wavelength effect. New PAL results from

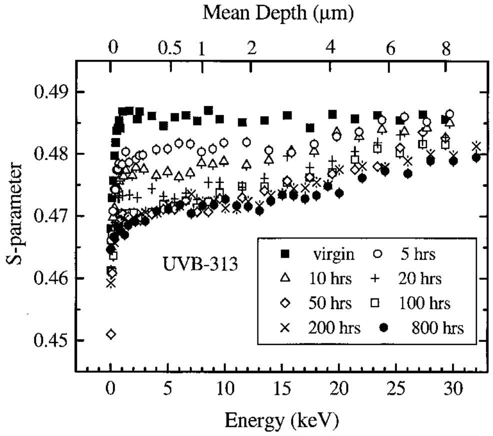

Figure 2. *S* parameter vs positron incident energy in polyurethane after different periods of UVB-313 exposure.

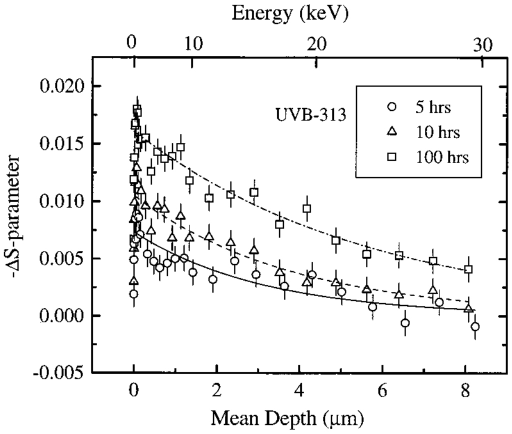

Figure 3. $-\Delta S$ vs mean depth in polyurethane after UVB-313 exposure. The lines are fitted by an exponential decay model (eq 2).

the PU coatings under these three types of UV irradiation conditions will be presented along with DBES and ESR data.

1. DBES Results of UVB-313 Irradiation. Figure 2 shows the *S* parameter vs positron incident energy and positron mean implantation depth (which is calculated from an equation in terms of positron incident energy and sample density[1]) for PU coatings treated by 5−800 h of UVB-313 irradiation in the energy range 0−30 keV. The rapid decrease in the *S* parameter near the surface (<1 keV) is a typical *S* parameter profile for polymeric materials. It can be interpreted as resulting from positrons diffusing back to the vacuum when implanted sufficiently close to the surface.[17] As seen in Figure 2, the *S* parameter systematically decreases with increasing irradiation time, which is consistent with the previous results. The reduction of the *S* parameter at any particular energy is calculated by the following equation:

$$\Delta S = S_t - S_0 \tag{1}$$

where S_0 and S_t are the *S* parameters of the virgin PU and the irradiated PU coatings with exposure time *t*, respectively. $-\Delta S$ is a parameter directly correlated with the structural changes in the material due to photodegradation. Figure 3 shows $-\Delta S$ after 5, 10, and 100 h of UVB irradiation vs mean depth and positron incident energy. The observations can be summarized as follows: (1) $-\Delta S$ is greater near the surface (except for the drop in the <1 keV region) and attenuates with depth; (2) $-\Delta S$ increases with increasing duration of UV irradiation. Smaller values of *S* or $-\Delta S$ at the surface in Figures 2 and 3 are due to an intrinsic feature of the slow positron technique. A significant fraction of back-diffused positrons at low implantation energy (<1 keV) reduces the fraction of positrons and positronium (Ps) atoms annihilated inside the material under study. Thus, a smaller value of *S* is observed at the surface with a skin layer about 40 nm. The decrease in $-\Delta S$ at depths larger than this skin layer can be explained by the attenuation of UV light intensity with depth. From the UV absorption measurements reported in the previous paper,[2] the PU coating shows strong absorption when the wavelength is smaller than 300 nm. The attenuation of light intensity follows Beer's law. Although the light source is polychromatic (280 nm $< \lambda <$ 390 nm), the overall effect can still be roughly expressed as a single-exponential decay function as shown by the lines in Figure 3 fitted from the data according to the following equation:

$$-\Delta S = -\Delta S_0 \times 10^{-\epsilon d} \tag{2}$$

where $-\Delta S_0$ is the $-\Delta S$ value at surface, *d* is the depth in μm, and ϵ is the extinction coefficient in μm^{-1}. ϵ is determined to be 0.14, 0.11, and 0.07 μm^{-1} for 5, 10, and 100 h, respectively. The decrease in the extinction coefficient with irradiation time indicates that the increase in $-\Delta S$ with time does not have the same increasing rate at different depth. The dependence of $-\Delta S$ on time for different depth will be discussed later.

Although the general observations of $-\Delta S$ vs depth and vs time for UVB-313 are similar to those for UVA-340 as reported in our previous paper,[2] the magnitudes are significantly different. To investigate the wavelength dependence of the irradiation effects, we plot $-\Delta S$ for 800 h UVB-313 exposure together with the result of 800 h UVA-340 exposure from our previous paper[2] in Figure 4. It is obvious that near the surface 800 h of UVB exposure results in a larger $-\Delta S$ than the UVA exposure. Near the surface, the magnitude of $-\Delta S$ for UVB-313 is approximately twice that from the 340 nm data. In Figure 4, we also plot the data for 10 h of Xe light irradiation (from ref 2). Degradation near the surface consistently increases with decreasing UV wavelength. The lines in Figure 4 (upper) are fitted by the exponential formula in eq 2. The fitted extinction coefficients are 0.03, 0.05, and 0.13 μm^{-1} for UVA, UVB, and Xe light data, respectively. As expected, the order is Xe light > UVB > UVA. The material has stronger absorption of the UV light with shorter wavelength. The fitted dotted line for the Xe light result is seen to be significantly off the data, especially in the low-energy region. This indicates that a single-exponential curve is inadequate to describe the Xe light intensity attenuation profile. Since Xe light has a broad spectrum approaching wavelengths as short as 250 nm, the polychromatic feature will lead to a significant deviation from Beer's law. An attempt using a two-exponential function as shown in the solid line of Figure 4 (upper) improves the fitting nicely. The fast decay component has an extinction coefficient of 1.3 μm^{-1}, which may correspond to a very strong absorption of the short wavelength part ($\lambda <$ 280 nm) of the Xe light. The other component has an extinction coefficient of 0.07 μm^{-1}, which is similar to the value for UVB (0.05 μm^{-1}). To see the relative effect of the three light sources, we

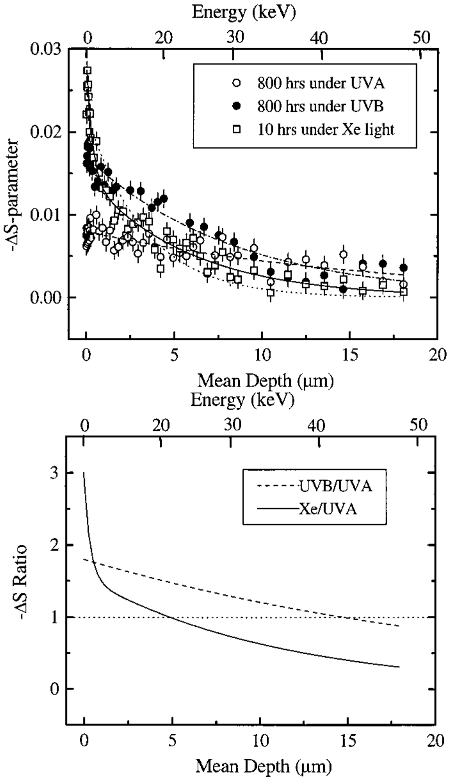

Figure 4. Comparison of $-\Delta S$ results of polyurethane after UVA, UVB, and Xe light exposure (upper) and the $-\Delta S$ ratio of UVB/UVA and Xe/UVA (lower) taken from the fitted lines in the upper plot. The dotted lines in the lower plot are drawn through 1 for comparison only.

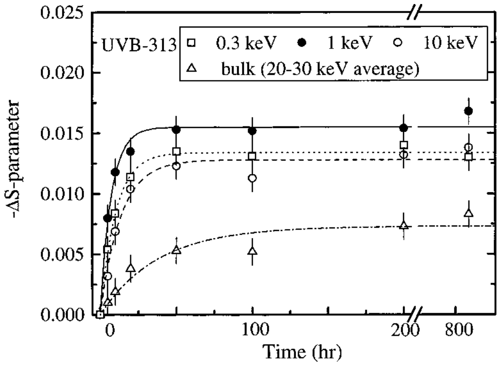

Figure 5. $-\Delta S$ vs exposure time for UVB irradiated polyurethane coatings at different positron incident energies. The lines are fitted by an exponential function (eq 3).

divide the fitted values of UVB and Xe light data by UVA fitted data and plot ratios of UVB/UVA and Xe/UVA in Figure 4 (lower). At the surface, the magnitudes of $-\Delta S$ due to Xe light and UVB-313 exposures are respectively 3 and 1.8 times as large as that due to UVA-340 irradiation. The effects are strongly depth-dependent. $-\Delta S$ values due to Xe light and UVB fall below that due to UVA at depths of ~5 and ~15 μm, respectively.

The variation in $-\Delta S$ with respect to time contains information about photochemical kinetics resulting from UV irradiation. In Figure 5, we plot $-\Delta S$ vs exposure time for different positron incident energies. The increase in $-\Delta S$ with time follows an exponential function (first-order kinetics) as follows:

$$-\Delta S_t = -\Delta S_{\max}(1 - e^{-kt}) \qquad (3)$$

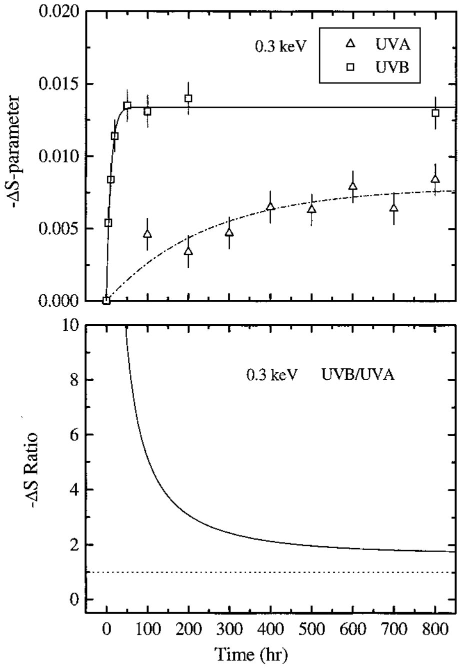

Figure 6. Comparison of $-\Delta S$ vs time at positron incident energy of 0.3 keV for polyurethane coatings after UVA and UVB irradiation (upper) and the $-\Delta S$ ratio of UVB/UVA vs time (lower). The lines (upper) are fitted to eq 3. The solid line (lower) is the ratio taken from the two fitted lines (upper). The dotted line (lower) is drawn through 1 for comparison only.

$-\Delta S_{\max}$ is determined to be 0.0134, 0.0155, 0.0128, and 0.0073 for 0.3, 1, and 10 keV and bulk (20−30 keV average) data, respectively. The $-\Delta S_{\max}$ value at 0.3 keV is smaller than the 1 keV value, which occurs for the same reason as the $-\Delta S$ drop near the surface in the depth profile plot (Figure 3) as explained above. $t_{1/2}$ (=ln 2/k) is calculated to be 7.0, 5.0, 9.2, and 26.2 h for 0.3, 1.0, and 10 keV and bulk data, respectively. $t_{1/2}$ is larger in the bulk than near the surface, which is consistent with observations from UVA and Xe light data.[2] One possible reason is that O_2, an important participant in photooxidation reactions, might have a concentration gradient with depth which may result in slower degradation in the bulk than near surface. The current results of 0.3 keV data from 313 nm irradiation are compared with those from 340 nm irradiation[2] in Figure 6 (upper). $-\Delta S$ increases much more rapidly with time for the shorter wavelength UV irradiation. The half-time of $-\Delta S$ from UVA-340 and Xe light results was previously reported to be 173 and 0.8 h, respectively, at an energy of 0.3 keV.[2] The irradiation effects of UVB and Xe light reach a saturation state ~25 and ~200 times faster, respectively, than those of UVA irradiation. The ratio of $-\Delta S$ from the exponential fitting values for UVB/UVA is plotted in Figure 6 (lower). At long times (approximately equilibrium state), the magnitude of the UVB irradiation effect is approximately twice that of the UVA effect.

It is worthwhile to note that positrons and Ps are sensitive to subnanometer defect structural changes of the local environment. This molecular level structural change starts at the very beginning of the photodegradation process as a result of chain scission and crosslinking.[10] The irradiated samples in our experiments show slight yellowness and embrittlement, but no obvious surface morphology change is observed. The PAS technique is able to characterize the early stage degradation before the macroscopic methods can detect any obvious mechanical property change. On the other hand, PAS is not necessarily directly correlated to the macroscopic deterioration of the coating materials such as strength loss, fading, chalking, and cracking, which are results of accumulated degradation over a long period. Although the $-\Delta S$ parameter from DBES almost reaches saturation in as short as 50 h under UVB-313 irradiation, the observed macroscopic deterioration may continue to much longer times.

The *S* parameter decrease after UV irradiation can be interpreted as being due to an overall decrease of free volumes and holes. A photooxidation mechanism for polyurethane degradation has been proposed from FTIR studies.[18] Free radicals initiated by the absorption of UV light react with O_2, forming peroxy radicals ($POO^{\bullet}$), which lead to very reactive oxy radicals ($PO^{\bullet}$) and then readily undergo chain scission. Chain scission could occur as a main chain scission or a cross-link scission.[18] The urethane cross-link ($-CH_2-NH-CO-OR-$) reacts with O_2, losing the hydrogen atom bonded to the carbon atom located in the α-position of the NH group and produces an oxy radical $-CH\dot{O}-NH-COOR-$. This alkoxy radical leads to the scission of the cross-link and forms an acid ($-COOH$) and a primary urethane group (NH_2COOR-). The scission of the cross-links is expected to enhance chain motion and increase free volume. But an increase of T_g and cross-link density of polyurethane after UV irradiation from dynamic mechanical thermal analysis (DMTA) was reported, which suggests a reduction in free volume.[18] The characterization of hole volume from the DBES results provides further evidence. It is believed that the recombination of radicals in the termination steps introduces extensive cross-linking reactions, which becomes the dominant effect leading to structural changes. The originally cross-linked polyurethane network turns into a more rigid, highly cross-linked structure.

The stronger effect of UVB-313 than UVA-340 irradiation is expected because photons with higher energy can initiate the free-radical chain reactions more effectively. The dissociation energies of some chemical bonds present in polyurethane are[19] 413 kJ/mol (C−H), 348 kJ/mol (C−C), 351 kJ/mol (C−O), 351 kJ/mol (C−N), 355 kJ/mol (N−H). The energy level of natural UV radiation (λ < 380 nm) is sufficiently high for the breakage of typical bonds in polymers after the photons are absorbed by impurities and unsaturated functional groups. But the energy required (290 nm) to break a C−H bond is at the edge of the natural UV and UVA-340 spectra, and its intensity is negligible. The UVB-313 light source with its spectrum ranging from 280 to 390 nm can readily break the chemical bonds and initiate the free-radical chain reactions. The dramatic Xe light irradiation effect is believed to be due to the presence of even shorter wavelength components (λ < 280 nm). Experiments using filtered Xe light irradiation with a cutoff at 300 nm were performed, and no obvious variation in the *S* parameter was found after 10 h of irradiation. Although light with a shorter wavelength can create more damage near the surface of the coating material, the effect attenuates more rapidly with depth due to the stronger absorption of the shorter wavelength light.

2. PAL Results. UV irradiation can affect hole size, fraction, and distribution, all of which can be determined using PAL experiments. PAL results from the PU samples exposed to three different light sources are presented and discussed below.

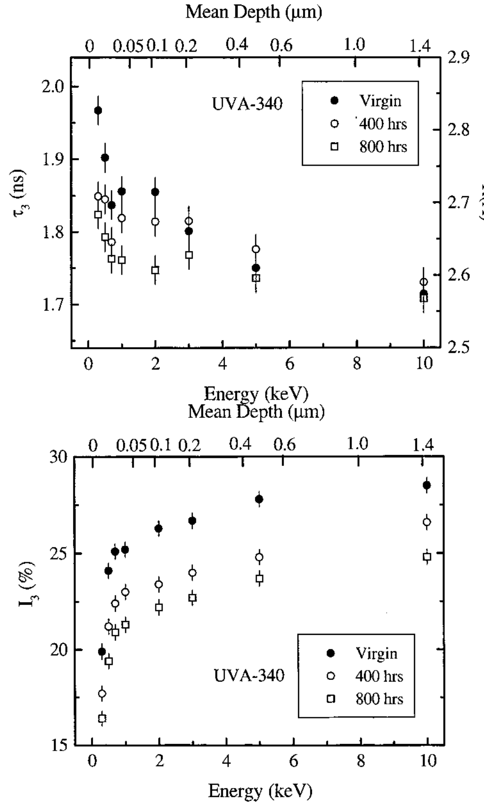

Figure 7. o-Ps lifetime (τ_3), mean hole radius (*R*), and intensity (I_3) vs positron incident energy in polyurethane after different periods of UVA-340 exposure.

a. UVA-340. The PAL spectra of the PU samples were analyzed into three lifetime components. The third lifetime component is attributed to the annihilation of the orthopositronium (o-Ps), which can be directly correlated with the holes and free volumes in polymers. The o-Ps lifetime (τ_3) and intensity (I_3) of the virgin and UVA-340 irradiated samples are shown in Figure 7. The decreases of I_3 and τ_3 near the surface are consistent with the previous studies.[17] Both τ_3 and I_3 decrease with increasing duration of UV irradiation. The mean hole size *R* (angstroms) can be calculated according to the semiempirical correlation between o-Ps lifetime and free-volume hole radius,[3] and it is labeled on the right *y*-axis of Figure 7 (upper). The o-Ps intensity I_3 can be used as a probe for the free-volume hole fraction if there is no strong Ps-inhibiting group present in the material. The free radicals generated in the photochemical reactions could be strong Ps inhibitors. But the DBES and PAL measurements were performed several weeks after the samples were taken out of the UV chamber, and the results are reproducible several months later. There is no direct effect from free radicals on the DBES and PAL data. The observed reduction in I_3 is interpreted as being due to decreases in free volume and hole fraction. Assuming I_3 is a measure of free-volume hole number, the fractional hole volume f_v can be calculated by an empirical equation,[6] and it is considered to be only a relative quantity. f_v is calculated and plotted in Figure 8. Both hole size and relative fractional hole volume decrease after UV irradiation. This indicates an increase in cross-linking due to UV irradiation. The magnitude of the f_v change ($-\Delta f_v$) is plotted in Figure 8 (lower). It has a similar trend to $-\Delta S$, decreasing with increasing

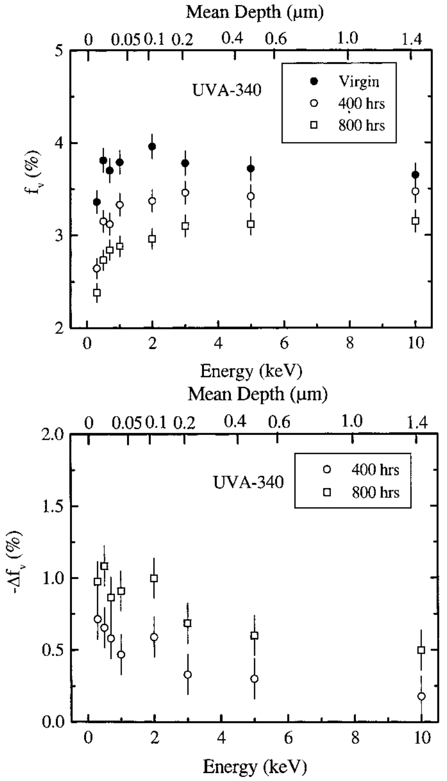

Figure 8. Fractional free volume (f_v) and $-\Delta f_v$ vs positron incident energy after different periods of UVA-340 exposure.

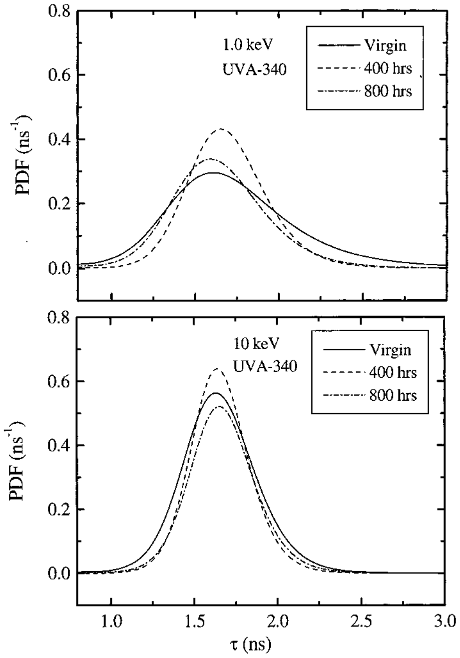

Figure 9. Probability density function (PDF) vs o-Ps lifetime for virgin and UVA-340 irradiated polyurethane coatings at positron incident energy 1.0 and 10 keV.

depth and increasing with exposure duration.

The free-volume hole size in polymers always has a distribution. Therefore, we also analyzed the PAL data by resolving the spectra into continuous lifetime distributions using the MELT program.[16] Figure 9 shows the probability density function (PDF) of τ for the o-Ps lifetime component. The lifetime distribution peaks for virgin and 400 and 800 h irradiated samples are compared at positron incident energies of 1.0 keV (upper) and 10.0 keV (lower). As shown in Figure 9, the peak position does not shift much after the irradiation, but the PDF peaks are observed to become narrower and their integrated intensities decrease with exposure time. The narrower o-Ps lifetime distribution indicates a more uniform hole size distribution after the irradiation.

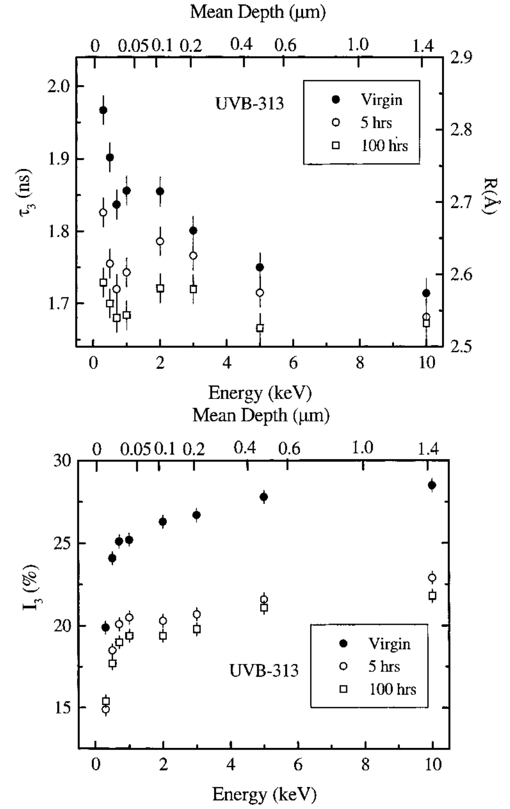

Figure 10. o-Ps lifetime (τ_3), mean hole radius (R), and intensity (I_3) vs positron incident energy in polyurethane after different periods of UVB-313 exposure.

b. UVB-313. Figure 10 shows τ_3, the corresponding R, and I_3 results from samples after UVB-313 irradiation. Significant decreases as a function of irradiation time are observed for both values. f_v and $-\Delta f_v$ are plotted in Figure 11. f_v undergoes ~50% decrease after 100 h of UVB irradiation. The maximum $-\Delta f_v$ of UVB results is ~1.5 times the UVA result near the surface, which is similar to the finding from $-\Delta S$ plotted in Figure 4 (UVB/UVA = 1.8 near the surface).

c. Xe Light. As observed from DBES results, Xe light shows the strongest effect on the PU coating in the near-surface region. Figure 12 compares the raw PAL spectra at a positron incident energy of 0.5 keV for samples after 1, 5, and 10 h of Xe light irradiation. A decrease of counts in a time range 2−10 ns in the spectra of the irradiated samples indicates a significant decrease of the third lifetime component. After 10 h of Xe light irradiation, I_3 decreases to be nearly negligible. It is worthwhile to mention that in all spectra there exists a long-lived o-Ps component in addition to three lifetime components analyzed. This long lifetime component appears to be independent of sample. It is probably due to back-diffused positrons and Ps annihilated in the beam chamber with a lifetime >10 ns but shorter than 142 ns (o-Ps lifetime in a vacuum). This long lifetime component is neglected by restricting the fitting range to <10 ns. The results of τ_3 and I_3 are plotted in Figure 13. As expected, a significant decrease in I_3 is observed.

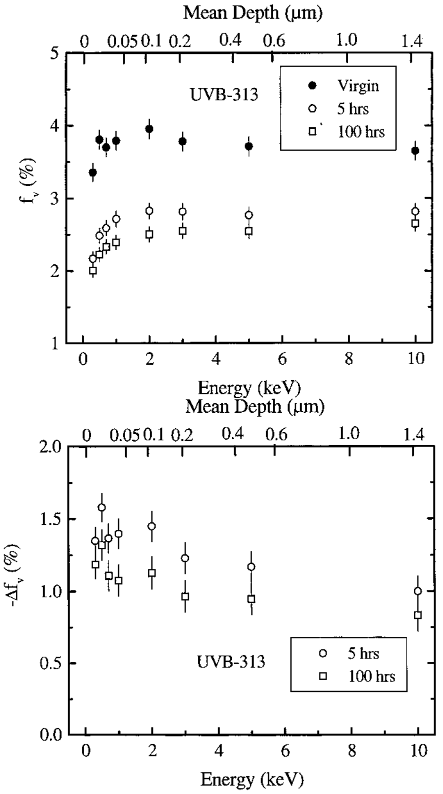

Figure 11. Fractional free volume (f_v) and $-\Delta f_v$ vs positron incident energy after different periods of UVB-313 exposure.

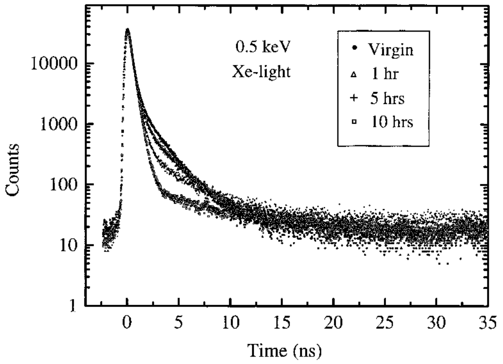

Figure 12. PAL raw spectra of polyurethane after different periods of Xe light exposure.

τ_3 appears to be more complicated. τ_3 increases after irradiation in the low-energy region (0.3, 0.5, and 0.7 keV), and the 10 h results are slightly larger than virgin data over the entire energy region. This abnormal increasing trend might be attributable to interference from the long lifetime component. The interference from the long lifetime component becomes more severe when I_3 dramatically decreases. In the case of small I_3, τ_3 is highly correlated with I_3 in the PATFIT analysis. In this case, the interpretation of τ_3 as hole radius due to Xe light irradiation needs to be more cautious.

f_v and $-\Delta f_v$ are calculated and plotted in Figure 14. f_v near the surface decreases to almost 0 after 10 h of Xe light irradiation. This indicates that a high cross-link-density network may have been formed even with a short period of Xe light irradiation. The highly cross-linked polymer matrix is more rigid. The PU coatings after Xe light irradiation were found to be hardened, brittle, and easy to detach from the Al substrate.

The maximum $-\Delta f_v$ in Xe irradiation results is ~3.5 times that of the UVA-340 result, which is similar to

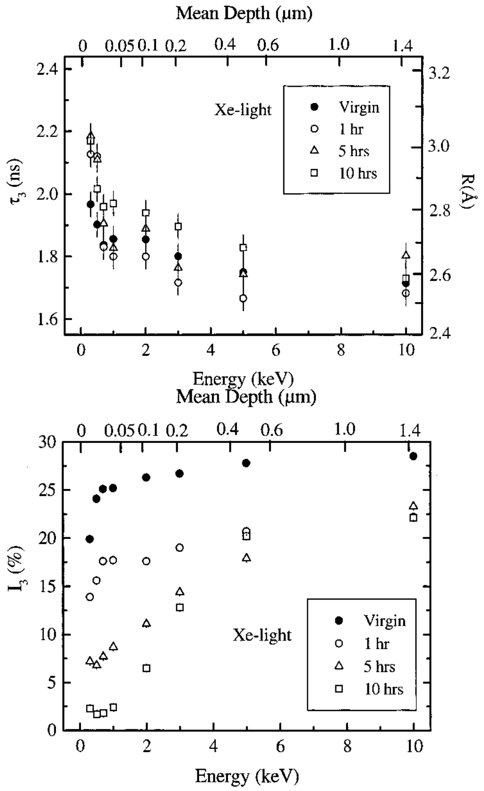

Figure 13. o-Ps lifetime (τ_3), mean hole radius (R), and intensity (I_3) vs positron incident energy in polyurethane after different periods of Xe light exposure.

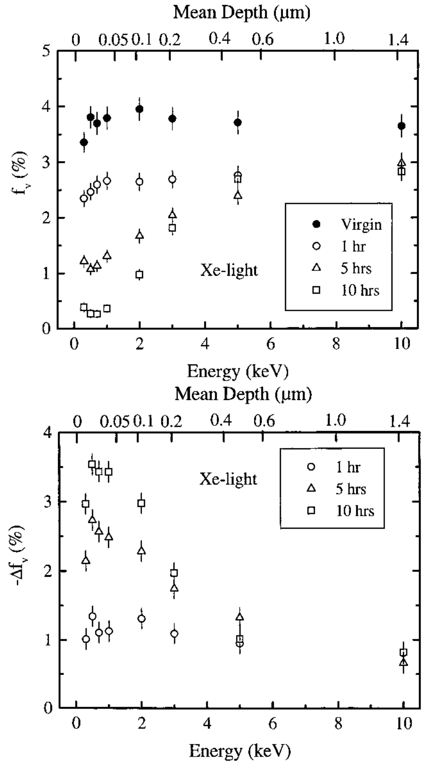

Figure 14. Fractional free volume (f_v) and $-\Delta f_v$ vs positron incident energy after different periods of Xe light exposure.

the $-\Delta S$ ratio of 3.0 from DBES results (Figure 4). $-\Delta f_v$ for Xe irradiation attenuates much faster than that from UVA and UVB results when approaching the bulk. This trend has been explained by the stronger absorption at shorter wavelengths. To compare DBES and PAL

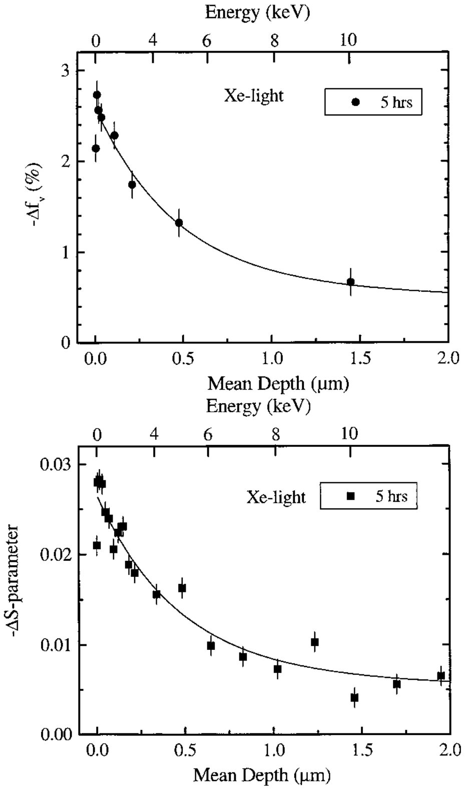

Figure 15. $-\Delta f_v$ from PAL and $-\Delta S$ from DBES vs mean implantation depth. The lines are fitted by the same exponential decay model.

results, $-\Delta f_v$ and $-\Delta S$ vs depth profiles for 5 h Xe light irradiated sample are plotted in Figure 15. A two-component exponential decay model is used, and exactly the same extinction coefficients are obtained: $\epsilon_1 = 0.92$ μm^{-1}, $\epsilon_2 = 0.03$ μm^{-1}. The initial ($d = 0$) values for those two components are determined to be 2.0 and 0.6 for $-\Delta f_v$ and 0.02 and 0.006 for $-\Delta S$. Both $-\Delta f_v$ from PAL and $-\Delta S$ from DBES are seen to follow the same depth profile.

3. ESR Results. A free-radical chain reaction mechanism has been proposed for photodegradation of polyurethane coatings.[18] A linear correlation between $-\Delta S$ from DBES and free-radical concentration from ESR for the UVA-340 sample series was reported in our previous paper.[2] ESR signals of the UVB-313 irradiated samples immediately after irradiation durations from 100 to 800 h were also recorded. Figure 16 shows the comparison of ESR spectra from PU samples after 400 h of UVA and UVB irradiation (upper) and the relative intensities (integrated area of ESR signal) of the UVA and UVB sample series. These particular ESR signals show few features that can be related to particular radical species. The spectra of the UVA and UVB samples have the same shape. But the signal intensities of UVB irradiated samples are significantly stronger than those of UVA samples. The average ESR intensity of UVB series is twice the UVA average intensity. The stronger effect of UVB is consistent with the positron results. This is interpreted as being due to the larger photon energy breaking chemical bonds more effectively and producing more free radicals. Although the positron technique measures permanent physical microstructural changes and the ESR technique detects transient free radicals related to the photochemical processes, a correlation can be established between those two. This is because photochemical reactions are the direct cause of both chemical and physical property changes in the material. These reactions ultimately lead to coating failure.

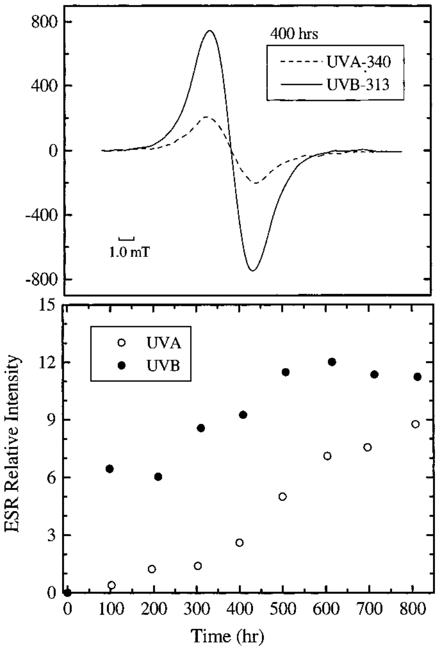

Figure 16. ESR spectra of polyurethane coatings after UVA and UVB exposures (upper) and the comparison of relative ESR signal intensity vs time for UVA and UVB irradiated polyurethane coatings.

Conclusion

The photodegradation of a polyurethane coating induced by three light sources with different wavelengths is studied by slow positron DBES and PAL methods. The *S* parameter from DBES and f_v obtained from PAL systematically decrease with exposure time. The hole size distribution is found to be more uniform after the UV irradiation. The UV irradiation effects are found to be strongly wavelength dependent: (1) the photodegradation effect induced by a shorter wavelength (313 nm) UV irradiation is 2 times as strong as that due to 340 nm UV irradiation near the surface; (2) the effects of the shorter wavelength UV attenuate with larger extinction coefficient when approaching the bulk; (3) the effects due to the shorter wavelength UV reach saturation much faster than those from the normal sunlight wavelength region. Both the DBES and PAL techniques are demonstrated to be sensitive tools to characterize the depth profile of microstructural changes of polymeric coating materials.

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