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Spectroscopic adsorption and effective dosage in accelerated weathering of a polyester-urethane coating

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Topcoat integrity is a crucial property for a protective coating system for protecting metal substrates in conjunction with anti-corrosion primers. Infrared spectroscopy was used to examine the chemical changes seen during accelerated weathering in a model topcoat urethane polymer and to measure the coating ablation. During weathering the ultraviolet absorbance of the urethane coating showed a typical tail (yellowing) into the visible region that increased with exposure period. Effective ultraviolet dosage can be calculated by integrating the spectrum of the incident radiation with the quantum yield for the degradation process and the ultraviolet absorption of the material under investigation. Depending on the form of the quantum yield, there is a clear acceleration of the absorption of damaging radiation because the absorbance increases with exposure. This non-linear relationship offers possibilities on how to estimate a service lifetime; one could choose a value of the exposure period characteristic of the start of the acceleration in dosage, or one might choose the asymptote at which the dosage rate becomes very great. The ultraviolet tailing into the visible region is analyzed as an example of an "Urbach" tail which is usually attributed to structural disorder that introduces energy levels between the principle electronic states. © *2002 Kluwer Academic Publishers*

1. Introduction

Polyurethane coatings have a deserved reputation for durability in withstanding aggressive environments. One such application is providing durable topcoats for equipment that is protected from corrosion by a suitable corrosion inhibiting primer. In such multi-coat systems, the overall integrity of the substrate and its survival depends crucially on the continuing integrity of the topcoat [1]. The topcoat provides a barrier to penetration by atmospheric moisture and the corrosive components of the atmosphere that may originate as pollution, in addition to any appearance related properties that may be required for the equipment or installation. Thus understanding the rate of degradation of urethane based coatings under attack by solar ultraviolet and the other elements of weathering is an important technological goal. Indeed, there has been a great deal of excellent work done in determining the chemical changes that occur during degradation of urethane coatings [2, 3, 4]. Much of the prior work determines the relative rate of appearance or disappearance of infrared bands in various polymers by comparison to another band, usually a carbon-hydrogen absorbance on the assumption that the CH band is a measure of the amount of polymer material that remains. Technologically useful polymers or additives may then be selected or designed by choosing the structure that suffers the least of these relative changes [5]. This work examines changes in the ultraviolet absorption during exposure, in addition to the infrared, in order to assess the amount of damaging radiation absorbed by the polymer, as well as follow the chemical changes.

2. Background

2.1. Determination of coating ablation and structural changes by spectroscopy

Infrared spectroscopy is a very valuable technique for determining the chemical changes that occur during weathering of polymeric materials. It has been used to compare the durability performance of complicated proprietary polymers and to determine the actual chemical reactions during degradation in polymers whose structure is known. Since there are several possible reactions in urethanes, and their progress may change with depth into the coating [6], for quantitative work it is necessary to make samples for examination that are as homogenous as possible and that can be examined in a straightforward manner. The polyester-urethane coatings were spin coated onto very polished, planar silicon or germanium disks. Neither silicon nor particularly, germanium have any absorption in the infrared spectral region of interest for most polymer degradation studies. Thus quantitative study of the urethane absorption may be achieved by standard transmission technique.

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Although each sample was marked so that the infrared beam would pass through the same location again after each exposure interval, spin coating was used to ensure smooth, level coatings so that minor registration errors would not have significant impact on the results.

An added aspect of the smooth, level coatings was that interference fringes were apparent in the spectra and could be used to measure the changing thickness of the coatings as they were ablated during degradation. Both silicon and germanium have high refractive indices and so reflect an appreciable amount of light. Similar fringing may be used in infrared spectroscopy for determining optical path length of cells for measuring liquids and gases and in establishing the parallelism of the end windows in such cells [7]. The fringe spacing is related to the optical path length between the reflecting surfaces by:

$$\Delta\nu = 1/(2dn) \tag{1}$$

where ν is the wavenumber; $\Delta\nu$ is the difference in wavenumber between successive fringe maxima, or minima; d is the thickness of film; n is the refractive index of the coating film.

Most polymers of widely different monomer composition have very similar values of refractive index, so it is plausible to assume that the overall refractive index of the polymer is insensitive to the chemical changes that occur during degradation. Thus the reciprocal of the fringe spacing is a measurement of the coating film thickness and changes in fringe spacing as a coating degrades will measure the changes in film thickness and thus the rate of ablation, i.e., degradation. Other, physical means of measuring thin film thickness, e.g., by dial gauge or micrometer or induction gauge are not nearly so sensitive or accurate as this interferometric method.

Further, when using changes in infrared absorbance height or area to follow the progress of the degradation chemistry, the values can be normalized by using the fringe spacing which is a measurement of the actual film thickness remaining. This has two, related advantages over using another infrared band, e.g., a C-H band, as a reference: Firstly, changes in the reference moiety's concentration may now be investigated in addition to the other changes and secondly, the changes in band size with degradation exposure become an absolute measurement instead of being a relative measurement and so permits greater level of understanding. This can all be determined from the infrared spectra, otherwise a separate experiment and calibration would be necessary to follow the changes in concentration with film thickness or mass during degradation [5].

The effect of ultraviolet radiation during the lifetime of a material depends on the spectral distribution of the radiation, its intensity, how much is absorbed by the material, and the quantum yield of the degradation process. This approach was taken to quantify this effective dosage and to determine its usefulness in estimating coating service life. Estimating product lifetime is a major technological and financial target for any user of construction or other materials since product development and maintenance costs are often very high. This article focuses on polymeric urethane coatings, but the approaches may be useful for investigating other products.

The effective dosage can be calculated, as in the equation below [8]:

$$d_{\text{eff}}(\lambda, t) = \int_{\lambda_{\min}}^{\lambda_{\max}} E_0(\lambda, t)\left(1 - 10^{-A(\lambda,t)}\right)\phi(\lambda, t)\, d\lambda \tag{2}$$

where d_{eff} is the effective dosage at a given time (W/m^2) (will vary and accumulate with exposure); $\lambda_{\max}$ and $\lambda_{\min}$ are the maximum and minimum photolytically effective wavelengths; $E_0(\lambda, t)$ is the spectral irradiance, from sun or QUV etc. (W/m^2/nm); $A(\lambda, t)$ is the coating absorption spectrum; $\phi(\lambda, t)$ is the quantum yield of interest; t is the exposure time; λ is the wavelength.

One can calculate the effective damaging dosage as it varies with exposure time. In fact, one can determine which parts of the coating adsorption spectrum are most important in the overall value. It is a quantity that incorporates the input (weather), the material properties (absorbance) together with an expression of the effect (quantum yield). If the effective dosage is an important parameter in determining service life, then either it will be found to be a controlling variable in some crucial performance property or it will itself show some trends that can be used to deduce the progress of degradation. It is easy to see how an analogous expression could be generated to include the damage expressed in another product attribute, the corresponding material property and the controlling variable in the weather, which may not always be ultraviolet radiation.

In determining the effective dosage of the adsorbed radiation, the possibility exists that it changes as the coating degrades since it is known from many studies of degradation chemistry that materials change as they degrade. Thus the equation above shows that it is necessary to know how the UV absorption and quantum efficiency of the crucial processes change. Only changes in UV adsorption are reported here.

3. Experimental details

3.1. Materials

Trimethylol propane (TMP) (Aldrich), neopentyl glycol (NPG) (Aldrich), adipic acid (AA) (Aldrich), isophthalic acid (IPA) (Aldrich), and hexane diisocyanurate trimer (HDI trimer) Desmodur N3300(Bayer) were used directly from the suppliers without further purification. The polyester was synthesized according to Table I with no catalyst in a ramp cycle: 1 hour at 160°C, 2 hour at 180°C, 2 hours at 190°C, 2 hours at 200°C, and hold temperature at 210°C until acid value diminished below 10. The reaction was carried out in a reaction

TABLE I Composition of polyester used to make the model urethane polymer network

Components	Molar ratio	Properties	
Neopentyl glycol	3	Acid number	8.95
Trimethylol propane	1	Hydroxyl number	166.5
Isophthalic acid	1.714	Mol. wt (No. avg.)	2899
Adipic acid	1.286		

kettle with nitrogen purge, mechanical stirrer, thermocouple, and partial condenser.

The polyester had an average of 5 hydroxyl functionalities per chain, and the ratio with isocyanurate was calculated to be 1 : 0.4, hydroxyl : isocyanurate. The films were only partially crosslinked in order to allow degradation within a reasonable period.

3.2. Application

The samples were prepared by spin coating at 33% solids, at 4000 rpm for 10 seconds on 12 mm silicon or germanium discs. The solvent was 40% methyl ethyl ketone and 60% 1-methoxy-2-propanol acetate. The spin coater was a model WS-200-4NPP/RV from Laurell Technologies Corporation.

3.3. Infrared spectroscopy

The infrared absorption spectra were obtained in transmission mode using a Nicholet Magna 850 Fourier transform spectrometer, FTIR. Substrates were polished silicon or germanium infra-red transmission windows, 13 mm diameter and 2 mm thick, available from Wilmad Glass. The technique is similar to that practiced by Van der Ven and Guerink [9]. These substrates are inert and dimensionally stable when exposed to the radiation, heat and moisture of the accelerated exposure environment used in this investigation as well as possessing suitable optical properties. Their size was chosen so that they fit into an atomic force microscope, AFM, as well as the FTIR; the AFM results will be reported separately. Each of the substrates was marked so that it could be put into the spectrometer at the same position with respect to the infrared beam after each exposure period. Since the coatings were spin coated onto these very flat substrates, they were quite insensitive to exactly where they were located in the beam until appreciable degradation had taken place.

Analysis of the fringe spacing was done by curve fitting the IR absorbance spectra with a sine-squared wave in the portion between the carbonyl region and the CH stretch region. Nearby absorbance peaks were fit to Lorentzian peak shapes. The films used here were sufficiently thin that there were only two or three fringe maxima to use and so using the standard peak finding options in the spectroscopic software to get the maxima spacing did not give very reliable results.

3.4. Degradation conditions

Although the ultimate application of the knowledge gained in this investigation is to estimate the service lifetime of such coatings in natural weathering, an accelerated exposure chamber was used. These chambers may not emulate natural exposure closely, but they do provide a controlled environment whereas natural exposure is variable and not completely reproducible, nor repeatable. The chamber used in this work was a QUV/SE made by the Q-Panel Company. The exposure of the panels was controlled in cycles according to ASTM D4587-91; the maximum coating temperature was 60°C for 4 hours under radiation from the UVA fluorescent lamps following a period of 4 hours with condensing humidity at 55°C. The substrates used had a small diameter so all the duplicates could be accommodated in a single holder fabricated to occupy the space normally occupied by one standard 75 × 150 mm panel.

3.5. UV spectroscopy

Coatings were applied on quartz slides from Chemglass Inc. at the same thickness that was used to examine infrared spectroscopic changes. A Cary 500 UV spectrometer was used to obtain the absorption spectra using a clean quartz slide to obtain the baseline. The very small constant baseline at visible wavelengths was subtracted from the whole spectrum as a correction for scattering. No other scattering correction was attempted since there did not seem to be a constant slope component to the spectra and no features that would provoke Tyndall scattering were apparent in the separate study by atomic force microscopy.

4. Results and discussion

4.1. Infrared spectroscopy

The relative change in thickness as determined by the reciprocal of fringe spacing, Equation 1, shows an approximately linear reduction with exposure period, Fig. 1. Results from several repeat experiments are shown in this and other figures. This reduction in film thickness appears to be at a rate of approximately 50% over ten weeks. There is some noise in the data since the coatings were thin and produced three or fewer fringes for the curve fitting, but such a linear relationship is also very characteristic of weight loss results [10, 11] wherever that approach is used to evaluate coating degradation. The linear reduction in the coating thickness implies that degradation and ablation occur in a steady manner from a layer that remains essentially equivalent as degradation proceeds, or that loss of material does not depend on the amount of material remaining in the film (over a time scale comparable with the one week interval between testing), perhaps because the coatings are thin. Diffusion limited degradation kinetics might show a non-linear loss of material as degradation proceeds. In any case, the material lost must be in low molecular weight fragments since it is fugitive and does not impede further erosion. Although these results do not have direct use in estimating a coating lifetime they are suggestive of some mechanistic approximations that might be applied to modeling the rate of degradation.

Multiplying peak area by fringe spacing shows how the concentration of CH and CO in the degrading films changes with exposure period, since this is equivalent, see Equation 1, to dividing by the remaining film thickness.

Fig. 2 shows how the carbonyl bands change in the infrared spectra, again there are several repeat experiments displayed here. Fig. 3 then shows how the concentration of carbonyl changes as calculated by the area of the peaks multiplied by the fringe spacing. The increase over 10 weeks is approximately 25%. As the exposure progresses, the data in this figure contain more variation, probably due to increased variation in degradation across each sample, and towards the end, there may have been microscopic locations that no longer

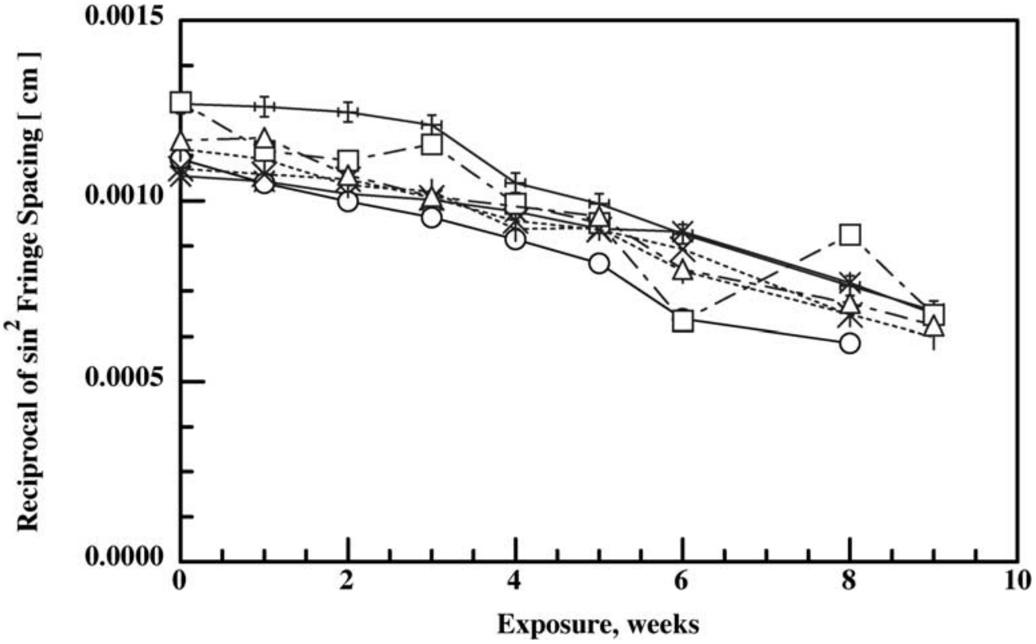


Figure 1 Change in coating film thickness with exposure period, determined by the reciprocal of fringe spacing [wavenumber, cm^{-1}] from infrared spectra. Each plot represents a repeat experiment.

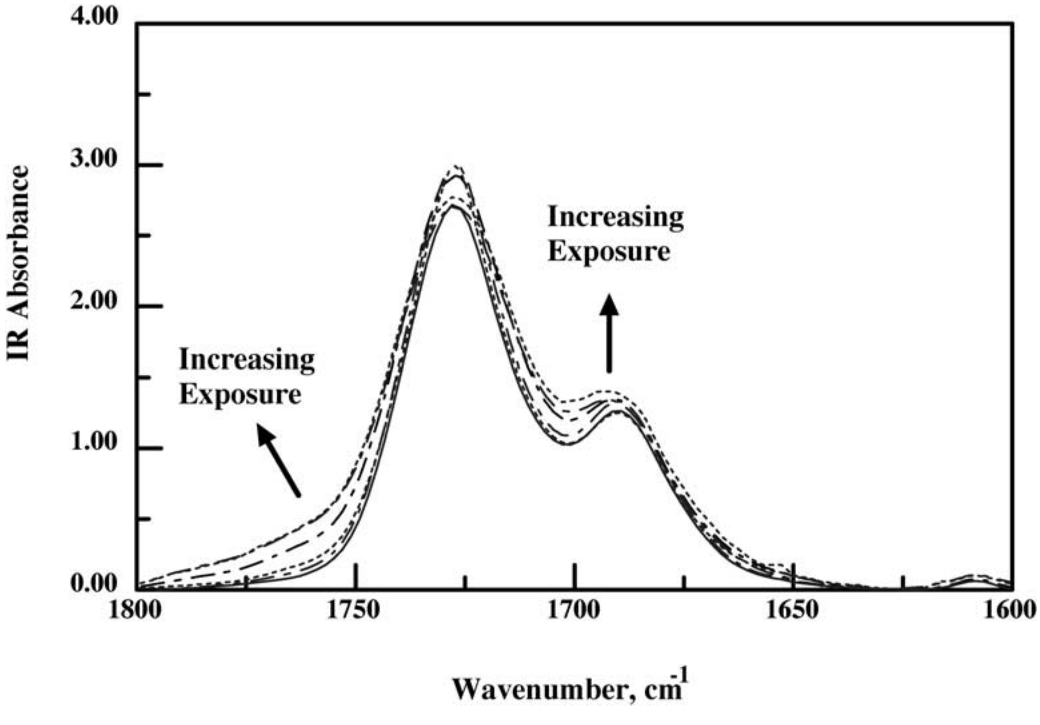


Figure 2 Infrared absorbance showing an example of how the carbonyl peaks change during the nine week exposure experiment.

had significant coating. Again, although there is some uncertainty in the data there appears to be a linear trend in carbonyl concentration.

Similarly, Fig. 4 shows that the CH concentration diminishes in a linear fashion at a rate that would be about 25% over ten weeks for all the experiments done here. The CH concentration diminishes with exposure period which shows that it would be unwise to use it as a normalizing factor in analyzing spectra without a separate calibration of film thickness. Changes in the CH concentration could easily mask another significant change if it were used unwittingly to normalize another band that changes with exposure.

For this polymer, there appears to be little that can be determined quantitatively in the OH, NH infrared spectrum around 3200–3600 cm^{-1}. Even if the (OH, NH) area is normalized using the fringe spacing there is no perceptible trend with exposure, even if the spectrum is fitted numerically and the contribution to the (OH, NH) area of the fringes is subtracted.

There are some general conclusions that can be drawn from the quantitative changes in thickness and composition. The thickness diminishes faster than the CH concentration is reduced, then the volatile fragments, on average, contain less CH than the previously intact polymer. Almost every polymer contains many more

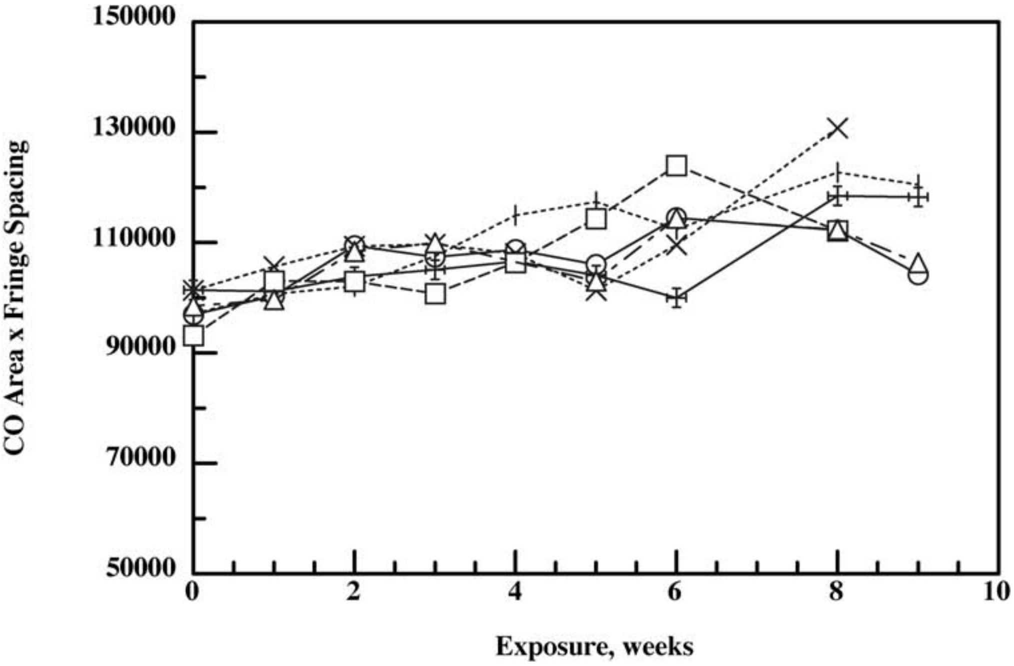


Figure 3 Change in carbonyl concentration during degradation from the infrared peak area and fringe spacing (for the same coating samples in Fig. 1).

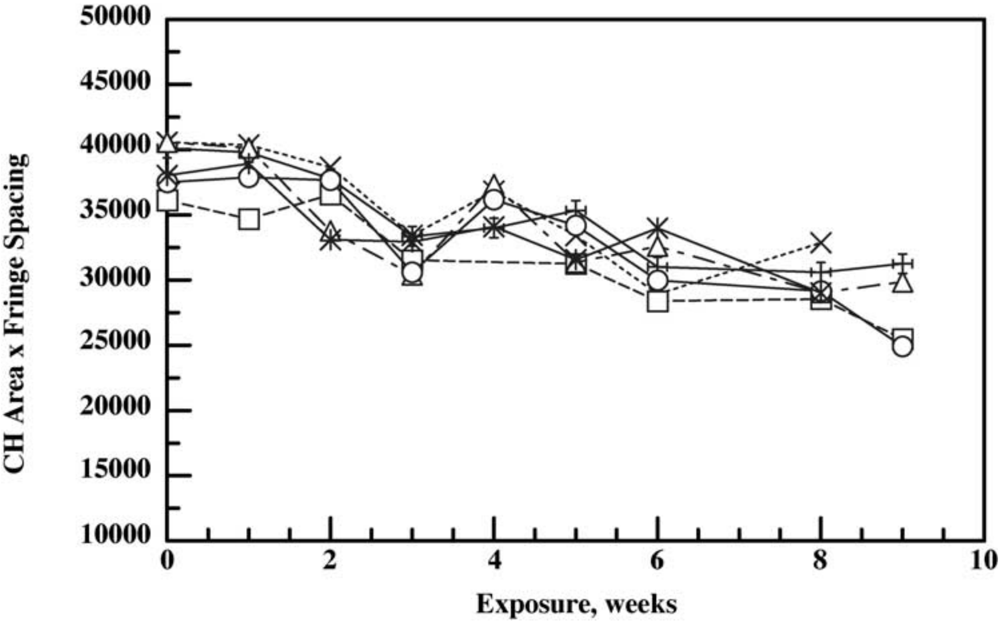


Figure 4 Reduction in CH concentration during degradation measured using the infrared peak area and fringe spacing (for the same coating samples in Fig. 1).

CH groups than other moieties. Thus it apparently requires only a modest fraction of the CH groups to be oxidized to CO for the CO concentration to increase. If the concentration of CH in the degraded film is reduced to 3/4 of its original concentration and the concentration of CO increases to 5/4 of its starting concentration, then the ratio in the degraded film should be 5/3 of its starting value which may represent a substantial change in the intermolecular environment. Inevitably, the chemistry of degradation involves more than the processes involved in the CH and CO absorbances, but clearly there are major changes within the coating.

4.2. Ultraviolet absorption

As in the quantification of the infrared results, the thickness change was used to adjust the UV absorption since otherwise it is reduced as the optical path length through the coatings was reduced by weathering erosion. Thus changes in UV absorbance were determined that were a function only of how the material was changing, see Fig. 5. Although three repeat exposure series were performed, only one is presented for the sake of clarity in Fig. 5. It was interesting to see that this procedure clarified a nearly isobestic point at 295 nm better than the data displayed when uncorrected for thickness.

If UV absorbance is included in measuring the damaging dosage see Equation 2, then how and why it changes as the polymer degrades becomes important, particularly if it forms part of the means of predicting service life.

The UV absorbance shows several features. A major short wavelength peak occurred at ∼210 nm, with

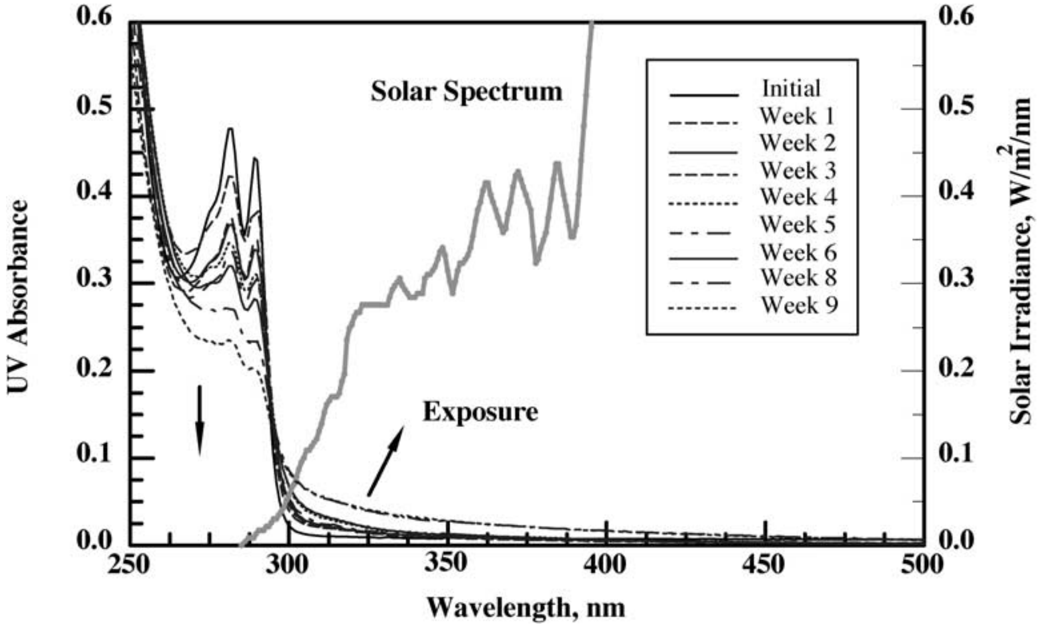


Figure 5 Ultraviolet absorption changes during exposure for a single coating in accelerated weathering, corrected for ablative thickness changes. Part of the solar spectrum is reproduced in the figure for comparison.

a shoulder around 240 nm, but initially the discussion will focus on that part of the absorption that falls within or close to the solar spectrum. Even without thickness correction, there is an absorbance tail into the visible region that is present in the pristine material and that increases with degradation (weeks of exposure) as the polymer yellows. The three peaks around 270–290 nm all diminish as the degradation period increases, but the underlying absorption at shorter wavelengths remains constant (when adjusted for ablation). Thus these peaks diminish by some mechanism that does not correlate directly with material loss. In the data here, the tail increased as degradation proceeded but without developing any appreciable, separate new peak. Yellowing is an extremely common phenomenon that is attributed to chemical changes. No visible turbidity developed and no features were seen in by atomic force microscopy that might produce Tyndall scattering so the discussion here will assume, as others have, that the tail is yellowing and was produced by chemical (electronic) changes and not purely physical features.

There are well documented cases of new chromophores generating obvious features in yellowing polymers [12, 13]. Any peak caused by a new chromophore could be broadened due to multiple vibrational states splitting the peak and broadening it, but one would expect a maximum to be apparent. It is commonly reported that such tails are the result of absorbing moieties being generated by the chemistry of degradation, but other workers have discovered increased tailing without a defined maximum appearing in the spectrum [14–16]. Such results, together with the observation that even those with a new maximum appearing also show a larger, underlying tail, increase the motivation for seeking mechanisms and descriptions for this behavior that do not necessitate particular chemical changes producing yellow chromophores.

The carbonyl region in infra-red spectra taken during degradation also showed a broadening, Fig. 2, which might be thought of as consistent with the broadening (yellowing) in the ultraviolet, since the peaks around 260–290 nm are usually attributed to carbonyl n-π^* transitions. These peaks are often seen in polyester–urethanes or acrylic polymers [17]. The three peaks in this region of the ultraviolet absorption are probably due to fine structure typical of transitions that are smoothed out in solid materials. Infrared carbonyl spectra show several vibrations of the appropriate energy to account for the splitting in the UV spectrum [18].

Conventional analysis of spectroscopic changes focuses on suggestions of specific chemical changes to account for change in spectral features. For example, the usual explanation of a reduction in UV intensity when a polymer is irradiated is that the chromophore is being destroyed by the radiation. Ultimately, that may well be true, but predicting the lifetime of a coating polymer requires knowledge of not only chemical changes but all processes that change the UV absorption. These samples were thin films, suitable for near UV transmission, and were eroding but not changing color perceptibly. Clearly, the encroachment of the blue end of the UV-visible spectrum in this model urethane corresponds to yellowing, and should be expected since urethanes are known to suffer yellowing. In conventional degradation studies, if a polymer "yellows," then the obvious change of color is used as a criterion of failure [15, 19]. Such specific chromophores may appear later as the chemical products of degradation become more concentrated but here these effects may be due to existing adsorption processes or materials that are altered only somewhat as degradation proceeds.

One of the differences between the infrared results and the UV spectra is that the carbonyl band area in the infrared increases in size but the UV peaks diminish, although the background UV absorption remains consistent with ablation. The peaks at 210 and 240 nm may also be attributed to carbonyl functionality [20], but would be the π-π^* peaks. Explanations for this

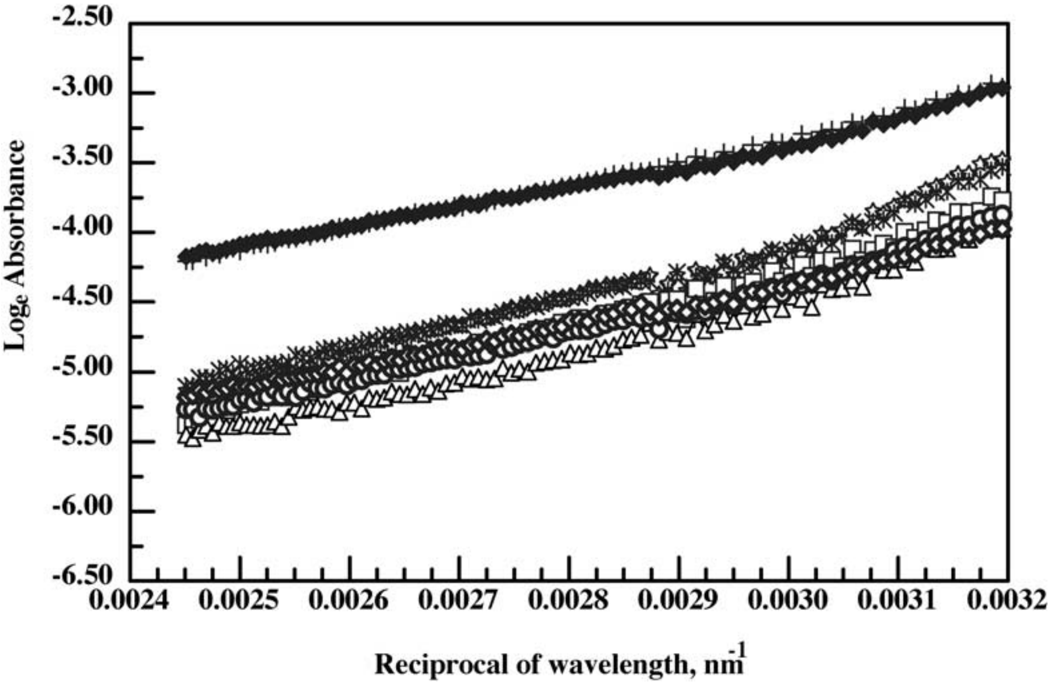


Figure 6 "Urbach" tail analysis of the ultraviolet spectra displayed in Fig. 5. The abscissa corresponds to wavelengths of 416 to 312.5 nm.

difference in behavior within the ultraviolet and between ultraviolet and infrared spectra are currently under investigation.

4.3. Ultraviolet absorption: Tailing

Instead of associating the ultraviolet yellowing tail with a specific spectral peak the absorption, α, in many materials varies exponentially with energy, as an "Urbach" tail [21], for energies below that corresponding to the central peak:

$$\alpha(\lambda) = \alpha_0 \cdot \exp\left[\frac{hc}{\lambda E_0}\right] \tag{3}$$

where λ is the wavelength; c is the velocity of light; h is the Planck's constant; E_0 is the energy value interpreted as the width of the tail of localized states in a band gap.

This equation was applied to the UV absorption obtained from the polyester–urethane polymer studied here (Fig. 6).

Linear regression of data in the diagram gave a characteristic energy, E_0, of ∼0.66 eV, which is consistent with literature values for polymers [22]. Usually, this exponential tail is attributed to thermal or structural disorder that provides electronic states that tail into the band gap for amorphous semiconductors [23]. Such analyses may give insight into the local molecular interactions that occur during weathering changes. The data do not display identifiable trends with increasing degradation in the characteristic "Urbach" energy, E_0, possibly because the ultraviolet spectra here were originally obtained to calculate the effective dosage, not optimized for examining the tail of the absorbance.

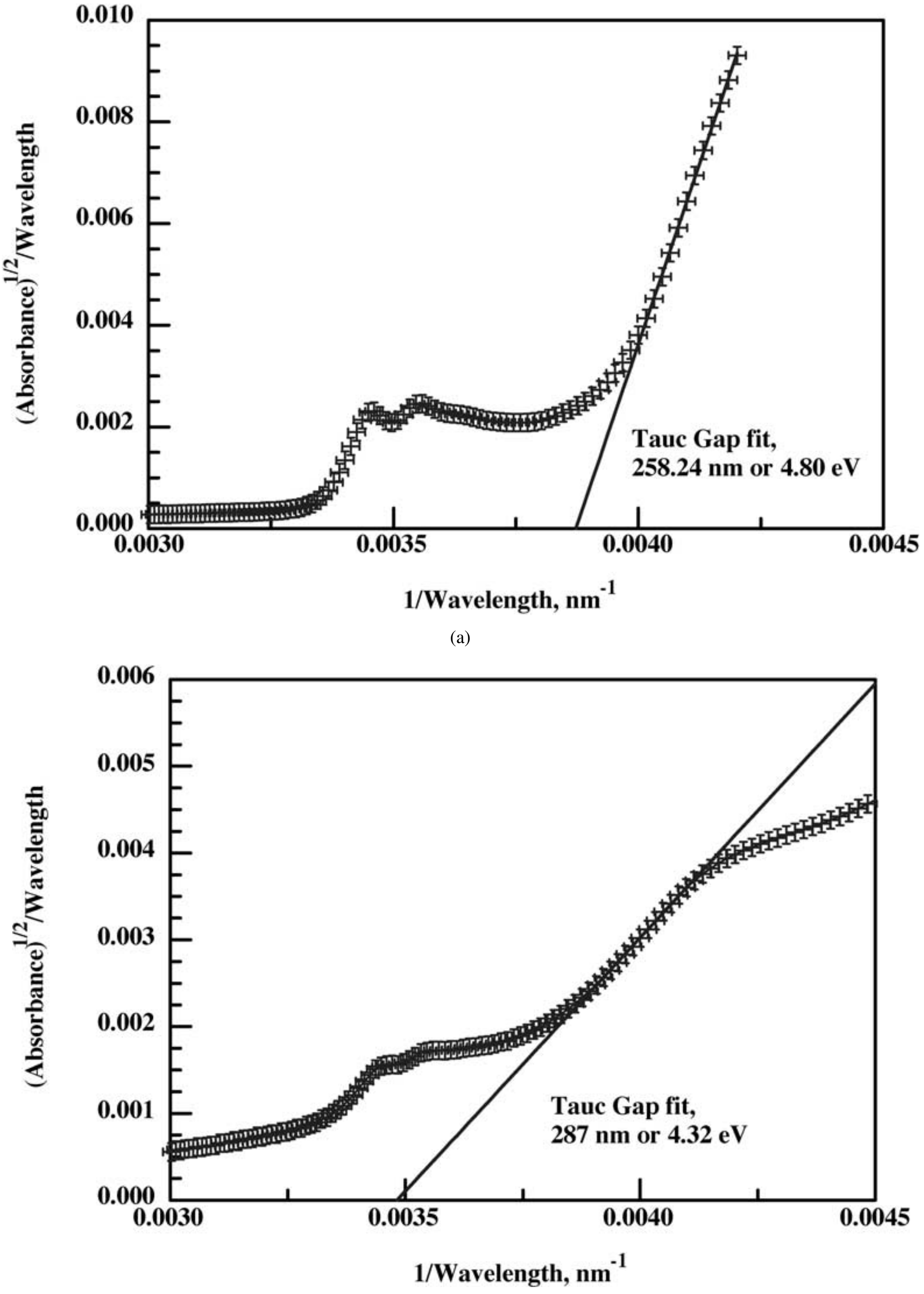
Urbach found this exponential tail behavior in inorganic halides but it has since been found for many materials including glasses and amorphous semiconductors. Whatever the exact mechanism is for this tailing, it must be a measure of a more complicated electronic density of states in which structural or compositional disorder perturb the molecular configurations.

One literature reference has been found for organic systems [22]. In that work, the energy, E_0, was approximately 0.3 eV, for organic asphaltenes, which is similar in value to that found here, 0.66 eV. In the studies where this relationship has been used, E_0 is construed as an energy that represents the width of the tail of localized states in the band gap and thus is much smaller than that band gap. The value of 0.66 eV found here, is small compared to values of band gaps typical of insulators such as these polymer films. If ultraviolet induced degradation produces long-lived free radicals for example, one might expect these unpaired electrons to provide electronic states within the band gap [24] and thus to contribute to fairly low energy electronic absorptions and thus UV tails. Since the UV absorbance tails examined here had the same value of E_0, within the uncertainty of the data, the increased UV-visible yellowing cannot be explained by changes in E_0. Thus, to be described by Equation 3, the changes must instead come from an increase in the pre-exponential term. A more complete form of Equation 3 includes a term, E'_{bg}, that is taken to be comparable to the appropriate band gap [25]:

$$\alpha(\lambda) = \alpha'_0 \cdot \exp\left[\frac{hc}{\lambda E_0} - \frac{E'_{\text{bg}}}{E_0}\right] \tag{4}$$

The same absorption spectra can be used to deduce a value for such a gap. Polymers are usually insulators that contain several different atoms, in a more or less random arrangement, so there is no easily identifiable bandgap as for a crystalline or amorphous semiconductor material. The n-π^* peaks at ∼250–290 nm seem much too small to be associated with this tail, however, one could chose a larger peak, i.e., at 210 nm, and calculate the corresponding energy, 5.9 eV (the deconvoluted peak with a center at 242 nm corresponds to an energy of 5.1 eV). This assumes that the tailing (yellowing) is a feature that is associated with these larger, short wavelength peaks. Inspection of spectra did not reveal a trend in the "210 nm" peak center with degradation period. This may be because the spectra were obtained with polymer films thick enough to obtain accurate values in the near visible region for the effective dosage calculation (see later) and these films have very high peaks centered around 210 nm so the spectrometer detector sensitivity and accuracy may be limited there.

An alternative approach is to employ "Tauc" gap analysis [26], an expression of the band gap used for amorphous semi-conductor materials. To use the Tauc approach, the square root of the absorbance divided by the wavelength is plotted against the reciprocal of the wavelength and the linear part is extrapolated to the abscissa to calculate the band gap energy of the amorphous material (Fig. 7). Here the value was found to



(a)

(b)

Figure 7 (a) "Tauc" plot of the ultraviolet absorption for unexposed polyester urethane; (b) "Tauc" plot of the ultraviolet absorption for the polyester–urethane after nine weeks of accelerated weathering exposure.

be 4.8 eV for the unexposed polymer, diminishing to 4.3 eV in exposed material. This magnitude is typical found for other polymers [24, 27] and is somewhat lower, naturally, than the energies deduced from the peak centers. The major linear part in the Tauc plots occurred at wavelengths around 250 nm (see figure below) so it is the gap derived from the resultant of the peak ~242 nm and the stronger absorption that peaks around 210 nm. It was difficult to identify a linear portion in Fig. 7 corresponding to those small peaks at 250–290 nm and thus get a good extrapolation to the abscissa for a "Tauc gap" for these transitions.

One can question whether Tauc gap analysis is appropriate to polymers under such conditions since polymer absorption is usually a succession of peaks and not an adsorption edge, but at least it is another quantification for comparing to the Urbach energy. It shows that E_0 is a suitable, small fraction of an energy that probably represents a lower bound on a characteristic electronic transition as expected from Equation 4. An advantage here is that the "Tauc" gap is derived from the long wavelength side of the π-π^* peak and so, again, may be connected to the processes governing the yellowing. In fact, an alternative view for the utility of the Tauc analysis is that it might provide a consistent way of characterizing how these peaks either move or spread on the longer wavelength side as the degradation proceeds. Since the Tauc gap apparently moves slightly to lower energies as the degradation proceeds, it means that the peaks may be moving or spreading to lower energies and may thus contribute to the increased tailing. Unfortunately, selecting the "straight" part of the Tauc plots for the extrapolation is somewhat arbitrary and the extrapolation to the abcissa will be sensitive to the quality of the baseline in the original data, thus any conclusions drawn from the data must be tempered with practicality.

Since the model polyester–urethane gave "Tauc gap" energy values that appeared to diminish a little with exposure it would make the tailing absorbance increase in Equation 4 as required by the experimental results. Indeed, the transition modeled by the "Tauc gap" may be sensitive to the intermolecular disorder and diminish as the disorder increases [23] and thus be consistent with the overall picture here.

Although higher energy absorbance peaks are more distant from the solar UV-visible range, they could be very important in defining the response of the material because they may be major contributors to the origin of ultraviolet tailing. Explanations of yellowing that require development of new chromophores are frequently allied to infrared analysis of degradation chemistry [28]. Such analyses find infrared bands that are attributable to species developed as the degradation develops. These new species then produce smooth featureless adsorption at the blue end of the visible adsorption spectrum so that the material yellows [29]. The ideas presented here would account for such a smooth tailing, or yellowing, without the formation of specific chromophores and would account for it before the degradation chemistry develops to the point where new "yellow" moieties are present at sufficient concentrations to provide a maximum in the ultraviolet absorption.

4.4. Ultraviolet absorption: Effective dosage

In order to properly measure the effect of UV exposure from Equation 2, one needs the quantum yield for the degradation process. There are very few data in the literature on quantum yields of degradation for suitable polymers that give any wavelength dependence. However, idealized data, most recently published by Bauer [30], can be used for discussion although there is no information on changes that may occur as degradation chemistry progresses. When a calculation of effective dosage was performed with this quantum yield data, the UV absorption determined here and the solar spectrum, the results showed little trend with exposure time (weeks), see Fig. 8. Another calculation was carried out using the same values of UV absorption and solar spectrum but by setting the quantum efficiency to unity at all wavelengths and exposure periods since it is, in truth, unknown. This second calculation showed a greatly increasing dosage rate with exposure since the absorption tail increases with exposure. The points in Fig. 8 were calculated for each week of exposure and the line segments merely join those points.

Clearly, the nature of the quantum yield has a crucial rôle in determining the damaging UV dosage. The shape of the curves is very significant. Depending on the form of the quantum yield, there is a clear acceleration of the effect of damaging radiation. This nonlinear relationship itself offers some possibilities on how to assess a service lifetime; one could choose a value of the exposure period characteristic of the start of the acceleration in damage, ~4 weeks in this case, or one might choose a value that represents the asymptote as the damage rate increases greatly, ~10 weeks here. This is somewhat analogous to choosing a "yield" point or ultimate value of stress in mechanical properties of polymers.

A crucial part of the ultraviolet absorption lies within the solar spectral range and is increased by degradation processes leading to further increased UV energy absorption and an accelerating rate of degradation. The response of the system to stimulus is to change its response so that it responds to a greater degree (positive feedback). A very simple algebraic model of this feedback might be:

$$d_{\mathrm{eff}}(t) = \frac{d_{\mathrm{eff}}(0)}{1 - k \cdot t} \tag{5}$$

where t is the exposure period; $d_{\mathrm{eff}}(t)$ is the effective dosage as calculated from the experimental results using Equation 2; $d_{\mathrm{eff}}(0)$ is the initial effective dosage, $t = 0$; k is the parameter discussed below.

In electronic circuits, very similar equations are used to calculate amplification controlled by feedback. This equation represents an increasing dosage rate that tends towards infinity at an exposure period of $1/k$. Further, it is easy to see that a graph of $d_{\mathrm{eff}}(0)/d_{\mathrm{eff}}(t)$ plotted as a function of exposure would be linear and have a slope

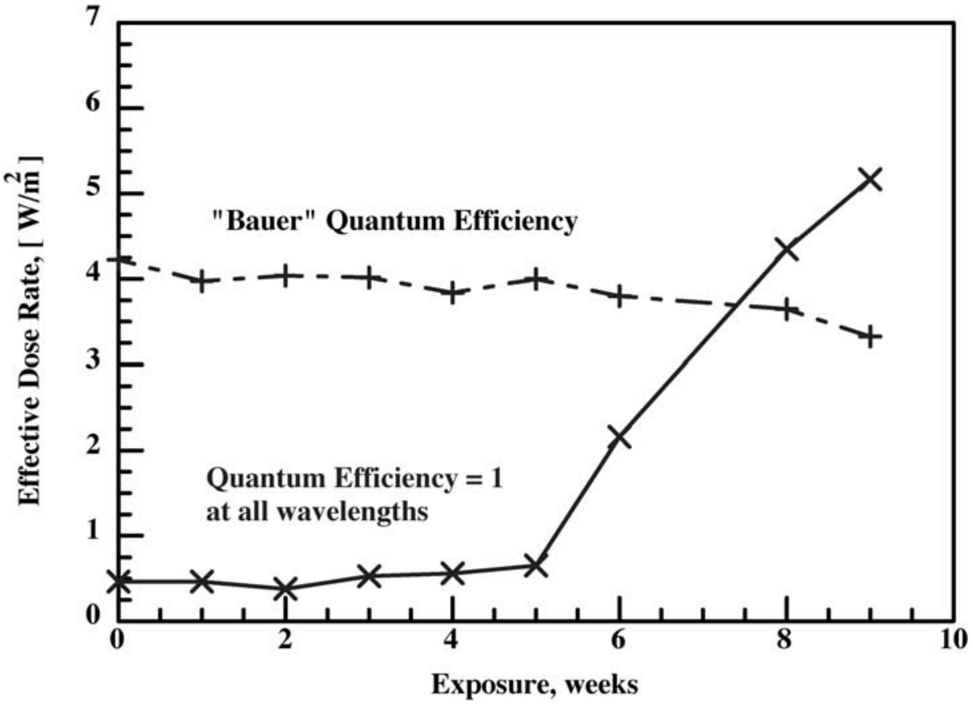


Figure 8 Effective dose rate calculated for exposure to the solar spectrum and showing the effect of quantum efficiency function.

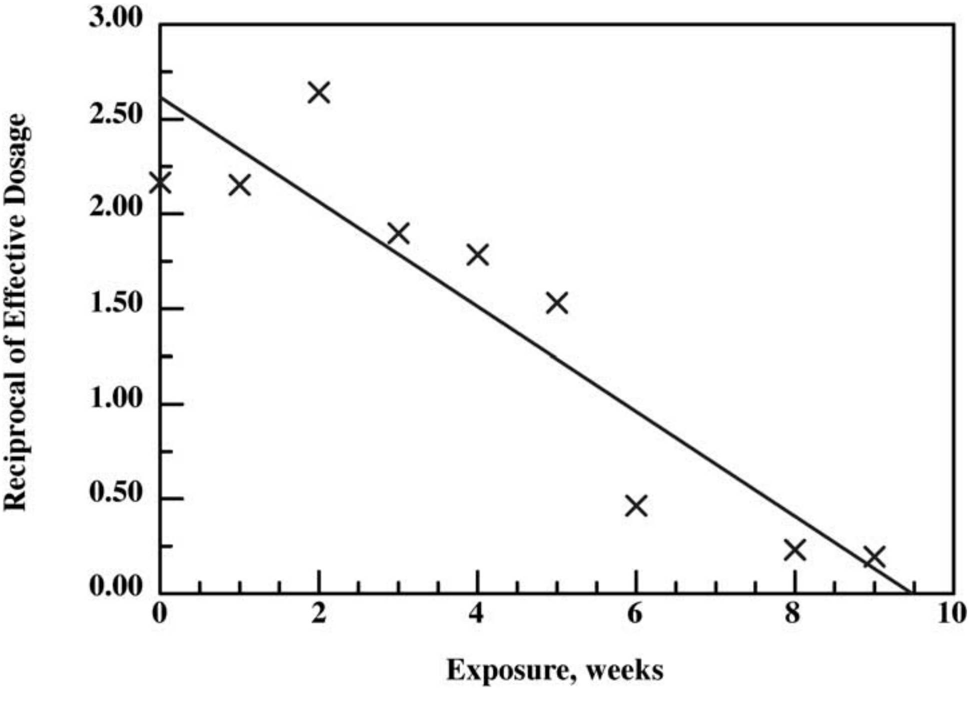


Figure 9 Reciprocal of effective dosage rate as a function of exposure period when the quantum yield is a constant (=1).

of $-1/k$ and an intercept on the exposure period axis of $1/k$. The parameter, k, in this very simple equation represents the reciprocal of what might be construed as the ultimate (not necessarily useful) lifetime of the material.

A simple test of this approach was done with the reciprocal of the effective dosage data calculated from the previous work and is presented in Fig. 9. There are perhaps too few data points in Fig. 9 for any strong conclusion, but if such a simple expression were found to describe the trend of effective dosage with exposure then careful experiments would allow an early estimate of the ultimate life. Although it is unlikely that such a simple relationship will prove to be applicable, understanding the shape of the non-linear response curve will be a valuable step in being able to estimate lifetimes. Further modeling techniques will be applied as more data become available.

Polyester and polyester components may react with atmospheric oxygen during weathering to form carbonyl or peroxide groups after main chain scission. The photo-initiated oxidation produces peroxides, ketones and aldehydes, and further photo-oxidation of peroxides and ketones yields peracids, which continue the oxidative degradation as oxidants [31]. If the ultraviolet adsorption is controlled by the carbonyl groups in this polyester-urethane and the result of weathering is to produce more carbonyls, as indicated in the infrared results, then the "feedback" process can be attributed to the carbonyl content of this polymer. In any case, any polymer that shows yellowing is a candidate for accelerating photolysis depending on how the quantum efficiency of the processes depends on wavelength and exposure.

5. Conclusions

Carbonyl concentration increases with degradation in polyester–urethane coatings as they oxidize as measured by infrared spectroscopy here and by many other workers, but the corresponding n-π^* transition peaks in the UV absorption measured here diminish as the degradation proceeds. This dichotomy needs further investigation and may involve loss of material containing carbonyl groups and oxidation of other parts of the polymer that remain.

Using the Fourier transform infrared spectrometer as an interferometer is a viable method of measuring film thickness and ablation during exposure. Infrared results show that film thickness diminishes and the CH concentration diminishes at different rates so the material remaining contains less CH than the original polyester–urethane. Thus remembering that the CO concentration shows a net increase (by infrared) means that the internal molecular environment must change considerably.

The absorbance tail into the longer wavelengths of the UV-visible region increases with degradation (weeks of exposure) and is clearly a major contributor to values calculated for the effective radiation dosage absorbed by the polymer. This encroachment of the blue end of the UV-visible spectrum in this model urethane corresponds to yellowing, and should be expected since urethanes are known to suffer yellowing. An explanation of "yellowing" that does not require specific degradation chemistry may be that it results from a broadening and diversification in the electronic transitions associated with existing groups on the polymer. As the polymer is oxidized and degrades, the local intermolecular environment around the chromophores changes and spreads the transitions over a greater range. This may describe yellowing that occurs before chemical degradation reaches the point of creating new structures that would provide chromophores in the visible region.

An exponential form fits the UV tailing well and was used to calculate a value, 0.66 eV, for the "Urbach" energy, characterizing the smearing of electronic energy levels within the transition gap corresponding to the main UV absorption. This energy parameter does not appear to change with exposure in this material, but the increase in tailing may be better accounted for by the value of the transition gap being reduced slightly as degradation continues. Other analyses, such as the approach of Tauc *et al.* may be useful as a quantification of the spreading of the larger UV peaks centered around 242 nm and 210 nm.

Since the ultraviolet absorption $\sim$210 nm is large, and if the increased tailing during degradation derives from existing features rather than from new chromophores, then it seems that the major contribution to the tailing would be from these peaks or other peaks at even shorter wavelengths, rather than from the much smaller n-π^* peaks that are close or within the solar spectral region.

Depending on the form of quantum yield as a function of wavelength, effective UV dosage absorbed by the polyester–urethane coating accelerated as the coating degraded, similar to a "positive feedback" response. For this coating, and others with carbonyl functionality that oxidize further, the positive feedback in the effective adsorbed dosage may well be controlled by the presence and absorption of the carbonyls. The form of the acceleration lends itself to some choices that could be used to define the lifetime of the coating in terms of the rate of radiation absorption. One could choose a point at which the adsorbed dosage accelerates noticeably, or one could extrapolate to a point when adsorption of UV radiation has increased to an extremely large value. In this polymer, any feedback process, if it exists, may be determined by the concentration and UV absorbing properties of carbonyl groups. If the causes for any non-linearity in the dosage response of a polymer as it changes due to degradation can be understood, then the functional form of the non-linearity may be deduced and thus bring prediction of service lifetime closer to reality.

Knowledge of the wavelength dependence of the quantum yield is very important in determining how much the individual UV adsorption peaks contribute to the radiation adsorption and is the subject of investigation. However, it is important that further attention is given to quantifying the exponential tailing (yellowing) that extends into the visible region because it is a major factor in energy adsorption regardless of the details of the quantum yield.

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