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# Quantitative Use of Ultraviolet Spectroscopy to Calculate the Effective Irradiation Dosage During Weathering

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**Summary:** The ultraviolet absorbance of a urethane coating showed typical yellowing that increased with exposure period. An effective dosage was calculated from the solar spectrum, the quantum yield for the degradation process and the ultraviolet absorption. Assuming a constant quantum yield, there is a clear acceleration of the absorption of damaging radiation because the ultraviolet absorption increases with exposure. This non-linear relationship offers possibilities on how to estimate a service lifetime. In addition, the yellowing can be analyzed as an "Urbach" tail which is usually attributed to structural disorder that introduces energy levels between the ground and excited electronic states.

**Keywords:** degradation, quantum yield, lifetime, Urbach, UV-vis spectroscopy

## Introduction

There has been substantial work done on the chemical changes that occur during degradation of urethane coatings[1,2]. Much of this 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 assuming that it is a measure of the amount of polymer material that remains. Polymers or additives may then be selected by choosing the structure that changes least[3].

The effect of ultraviolet radiation depends on the spectral distribution of the radiation, its intensity, how much is absorbed by the material, and whether any damage is done by a particular photon, i.e. the quantum yield of the degradation process. This research was done to quantify effective dosage and to determine its usefulness in estimating coating lifetimes. Effective dosage can be calculated[4]:

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

$d_{eff}(t)$ = effective dosage at a given time [W/m2] (will vary and accumulate with exposure)
$\lambda_{max}$, $\lambda_{min}$ = maximum and minimum photolytically effective wavelengths
$E0(\lambda,t)$ = spectral irradiance, from sun or other source etc. [W/m2/nm]
$A(\lambda,t)$ = coating absorption spectrum
$\phi(\lambda)$ = quantum yield of interest
$t$ = exposure time
$\lambda$ = wavelength

One can calculate the effective damaging dosage as it varies with exposure time and which parts of the coating absorption spectrum are most important. It is a quantity that incorporates the input (irradiation), the material properties (absorbance) and an expression of the effect (quantum yield). An analogous expression could be generated for another form of damage, the corresponding material property and another controlling variable in the weather, e.g. humidity. The equation shows that it is necessary to know how the UV absorption and quantum efficiency of the crucial processes change.

## Experimental Details

### Polyester Synthesis

**Table 1. Composition of polyester used in 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 | | |

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 as supplied. The polyester was made under nitrogen, synthesized with no catalyst: 1 hour at 160°C, 2 hour at 180°C, 2 hours at 190°C, 2 hours at 200°C, then held at 210°C until the acid value diminished below 10. The polyester had an average of 5 hydroxyls per chain, and the ratio of polyester:isocyanurate was 1:0.4.

By limiting the amount of cyanurate, this model system was crosslinked mainly through the primary hydroxyls on the polyester in order that it degrade within a practical period.

### Sample Preparation

Transmission infrared absorption spectra were obtained using a Nicholet Magna 850 spectrometer. Substrates were polished silicon transmission windows[5]. These substrates are inert in the exposure environment used in this investigation as well as possessing suitable optical properties. 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 they were insensitive to their exact location in the beam and being very flat and parallel-faced they produced fringes in the infrared spectrum that could be used to monitor their thickness.

Spin coating was done at 33% solids, in a model WS-200-4NPP/RV from Laurell Technologies Corporation. For ultraviolet spectroscopy, this material was applied thinly on quartz slides (Chemglass Inc). All the samples were cured for 2 hours at 120 °C in a convection oven so that there should be very little contribution from moisture curing to form polyurea; there was no spectroscopic evidence for unreacted isocyanate after cure. These coated specimens were then exposed in intervals of a week.

### Degradation Conditions

The exposure here used a QUV/SE chamber 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 x 150 mm panel.

### UV Spectroscopy

A Cary 500 spectrometer was used to obtain the spectra. The very small constant baseline at visible wavelengths was subtracted from each 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 a separate study by atomic force microscopy.

## Results and Discussion

A detailed discussion of the infrared analysis will be presented elsewhere. Change in fringe spacing was used as the measure of film thickness, so that the spectral changes could be corrected and quantitative deductions could be made. The carbonyl region, 1680 - 1730 $cm^{-1}$ increased as degradation proceeded, both in peak height and broadening of the peak at 1730 $cm^{-1}$; as expected, the films were being oxidized during the accelerated exposure. In fact, over the 10 week exposure period the carbonyl peak area increased by approximately 25%. During that period, the CH stretch region around ~2890 cm-1 diminished by ~25% while the overall thickness of the films reduced to ~50% of the starting value.

### UV Absorption

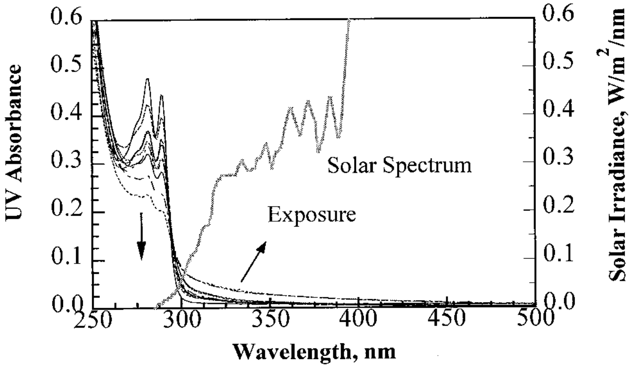

Figure 1. Ultraviolet absorption changes for a single coating in accelerated weathering, corrected for thickness changes. Part of the solar spectrum is reproduced for comparison.

Thickness changes measured from the infrared fringing was used to adjust the ultraviolet absorption so that it was function only of how the material was changing, see figure 1. Even without thickness correction, the absorption tail into the solar UV and visible region is present in the pristine material and increases with exposure. The peaks around 270 - 290 nm all diminish as the degradation increases. Here, the tail increased as degradation proceeded but without developing any appreciable structure. There are well documented cases of new chromophores generating obvious features[6, 7]; it is also commonly asserted that tails are the result of absorbing moieties being generated during degradation, but not always with any definite peaks being apparent[8, 9, 10]. Usually "yellowing," even with a new absorption peak includes a larger, underlying tail, so it is useful to seek mechanisms and descriptions for this behaviour that do not necessitate chemical changes producing specifically yellow chromophores. Predicting the lifetime of a coating polymer requires knowledge of not only chemical changes but any other processes that change the ultraviolet absorbance. The carbonyl region in infrared spectra taken during degradation also showed a broadening which is consistent with the tailing in the ultraviolet region, since the peaks around 260 - 290 nm are usually attributed to carbonyl n-π* transitions and are often seen in polyester-urethanes or acrylic polymers[11].

These samples were thin films, suitable for near ultraviolet transmission, and were visibly eroding but not changing colour perceptibly. Often, if a polymer yellows obviously, then the change of colour is used as a criterion of failure[9, 12]. It may be that the model polyester-urethane used here produced specific yellow moieties, but they were not concentrated enough to be perceptible.

### Ultraviolet Absorption: Tailing

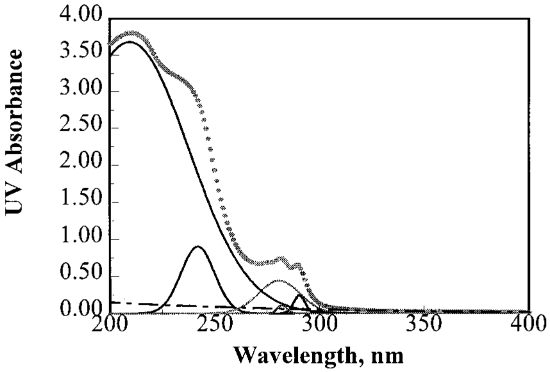

Figure 2. An example (eight weeks exposure) of the Gaussian peaks and exponential tail in the ultraviolet absorption of the polyester-urethane.

One can look elsewhere for an origin of the tailing phenomenon. Figure 2 shows an example spectrum, from a film that had been degrading for eight weeks. The figure shows the experimental data and Gaussian peaks, together with an exponential tail, that form an excellent fit to the data (the square of the regression coefficient > 0.9999). In order to match the data well, the tail had to be included when using Gaussian peak shapes. No reasonable choice of peak shapes could include the tail, although it might be part of a much larger peak that is centred at much shorter wavelengths.

The largest peak recorded was centred at ~210 nm. This peak has a much higher extinction coefficient and occurs at a wavelength where π-π* transitions, including those of carbonyl groups, are common[13]. Only the isophthalic acid component of the polyester had these peaks which also indicates that they are probably carbonyl.

The π-π* peak is so characteristically large that its own tail extends well into the visible, further than the smaller n-π* peaks. If one speculates that the tail originates from a larger, shorter-wavelength peak, then the speculation might include that only a minor broadening or shifting of that peak accounts for the increase in the tail as degradation proceeds. For energies below that corresponding to the central peak, there is an absorption tail in many materials that varies exponentially with energy, i.e. an "Urbach" tail [14]:

$$\alpha(\lambda) = \alpha_0^{'}.\exp\left[\frac{hc}{\lambda E_0} - \frac{E'_{bg}}{E_0}\right] \qquad \ldots 2$$

$E_0$ = construed as an energy that represents the width of the tail of localized states in a band gap

$E'_{bg}$ = electronic band gap energy

$h$ = Planck's constant

$\lambda$ = wavelength

$c$ = velocity of light

This equation was applied to the ultraviolet absorption spectra obtained from the polyester-urethane polymer studied here, figure 1. The exponential slopes appear not to vary with exposure period; linear regression gave a characteristic energy of ~ 0.66 eV, which is consistent with literature values for organic materials[15].

Usually, this exponential tail is attributed to thermal or structural disorder that provides electronic states that tail into the band gap[16]. Urbach found this exponential tail behavior in inorganic halides but it has since been found for many materials including glasses and amorphous semiconductors. The extended tail is a measure of a more complicated electronic density of states in which structural or compositional disorder perturb the electronic configurations. In polymers one would consider the transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital instead of a valence-conduction band gap. In the studies where this relationship, equation 2, 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 must be a fraction of that band gap. This value of 0.66 eV is much less than the typical band gap in an insulator.

Ultraviolet absorbance tails examined here apparently had the same value of $E_0$, so the increased UV-visible yellowing cannot be explained by changes in $E_0$. Thus the changes must instead come from elsewhere, for example the band gap term, $E'_{bg}$. One could chose a peak wavelength, 210 nm, and calculate the corresponding transition energy, 5.9 eV, or the deconvoluted peak with a centre at 242 nm (see figure 2) that corresponds to an energy of 5.1 eV. However, inspection of these data did not reveal a trend in peak position with degradation interval. This may be because the spectra were obtained with polymer films thick enough to obtain accurate values near the visible region, and they had very high absorbance centred around 210 nm, so the detector's sensitivity may be limited.

An alternative approach is to employ "Tauc" gap analysis[17], 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 abcissa to calculate the band gap [figure 3]. Here the value was found to be 4.8 eV for the unexposed polymer, diminishing to 4.3 eV as the urethane degraded. "Tauc gap" energy values that appeared to diminish a little with exposure would make the tailing absorbance increase in equation 3 as required by the experimental results. The magnitude of $E_{bg}$ is typical of other polymers[18, 19] and somewhat lower, naturally, than the energies deduced from the peak centres. The major linear part in the Tauc plots occurred at wavelengths around 250 nm so it is the gap derived from the resultant of the peak ~242 nm and the stronger absorbance that peaks around 210 nm. The arguments presented above suggest that the tailing cannot be associated with the small n-π* peaks, so the extrapolation was not done to deduce a "Tauc gap" corresponding to those peaks.

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. 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. It is characteristic of a π-π* transition to shift to longer wavelengths as its "solvent" environment becomes more polar which is consistent with a defining electronic transition, $E'_{bg}$, to shift to lower energies as a polymer oxidises.

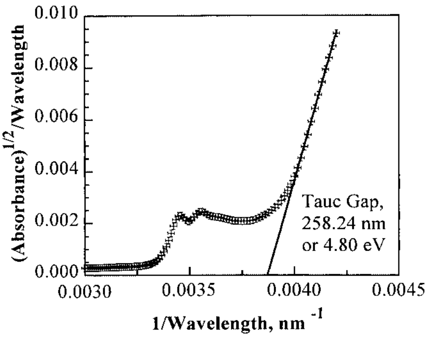

Figure 3. Example of "Tauc" plot of the ultraviolet absorption for unexposed polyester urethane.

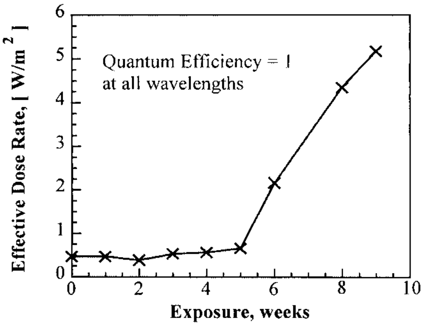

Figure 4. Effective Dose rate calculated for exposure to the solar spectrum with a constant quantum efficiency.

Explanations of yellowing that require development of new chromophores are frequently allied to infrared analysis of degradation chemistry [20]. Such analyses find infrared bands that attributable to species developed as the degradation develops. These new species then produce smooth featureless absorption at the blue end of the visible absorption spectrum so that the material yellows[21]. The ideas presented here would account for such a smooth tailing, or yellowing, without the formation of specific chromophores.

## UV Absorbance: Effective Dosage

In order to calculate the effective dosage, one needs the quantum yield for the degradation process. The calculation was carried out using the UV absorption (figure 1) and the terrestrial solar spectrum but by setting the quantum efficiency to unity at all wavelengths and exposure periods since it is, at present, unknown, but the subject of research. This calculation showed a greatly increasing dosage rate with exposure (figure 4).

Clearly, the nature of the quantum yield has a crucial rôle in determining the damaging UV dosage. There is a clear acceleration of damaging dosage. One could choose a lifetime corresponding to the start of the acceleration ~ 4 weeks in this case, or one might choose a value that represents the end, as the damage rate increases greatly, ~ 10 weeks here. This is somewhat analogous to choosing a "yield" point *versus* tensile strength in mechanical properties.

A crucial part of ultraviolet absorbance lies within the solar spectral range and is increased by degradation processes leading to further energy absorption and an accelerating rate of degradation. In such cases, the response of the system is to change its response so that it responds to a greater degree (positive feedback). A simple algebraic model of such feedback will be presented elsewhere.

The effective dosage calculation can be applied in determining the importance of the features in the UV spectrum separately. An example of the relative effect of each feature, from figure 2, is given in table 2 when it is used in equation 1 with the solar spectrum and suitable spectra for accelerated weathering chambers.

**Table 2. Relative contribution to Effective Dosage of each feature in the UV absorbance of polyester-urethane film. Example chosen was exposed for eight weeks in the QUV-340 chamber.**

| | **Solar** | **Xenon Arc with Borosilicate filter** | **Fluorescent UV-340** |
|---|---|---|---|
| Whole Spectrum | 1 | 1 | 1 |
| Peak at 210 nm only | $5\text{x}10^{-4}$ | $6\text{x}10^{-4}$ | 0.0012 |
| Peak at 242 nm only | $7 \text{ x } 10^{-11}$ | $3\text{x}10^{-10}$ | $1.2\text{x}10^{-12}$ |
| Peak at 281 nm only | $1.1\text{x}10^{-3}$ | $1.6\text{x}10^{-3}$ | 0.0012 |
| Peak at 282 nm only | 1.5 x 10-5 | $5\text{x}10^{-5}$ | $6\text{x}10^{-8}$ |
| Peak at 290 nm only | 3.3 x 10-4 | $5\text{x}10^{-4}$ | $7\text{x}10^{-5}$ |
| Exponential tail only | ~1 | 0.995 | ~1 |

Only the exponential tail contributes significantly to the calculation of the effective dosage, using a constant quantum yield. However, complete knowledge of the quantum yield is clearly very important in knowing the importance of a feature for the effective dosage of a material. One cannot discount the impact of a peak because its centre lies outside the irradiation spectrum cut-off. The table shows that the large peak at ~210 nm contributes as much as the smaller peaks closer to the solar region. This calculation also demonstrates that the borosilicate filtered Xenon arc spectrum is balanced closer to the solar spectrum than is the fluorescent UV-340, spectrum.

## Conclusions

Evidently, if the lifetime of a coating depends on the amount of UV radiation that it absorbs, then the short wavelength peaks cannot be ignored merely because their centre occurs outside the solar spectrum range. Equally, "yellowing" does not necessarily require chromophores centred in the yellow part of the visible spectrum, it could easily be tailing from a peak that is further into the UV.

Yellowing is clearly a major contributor to the effective radiation dosage calculation here but detailed knowledge of quantum yield is very important in determining how much the individual absorption features contribute and will be investigated further. A contribution to "yellowing" seems to come from a broadening and diversification in the electronic transitions associated with the polymer. Further chemical changes may be necessary to reach the point of creating visible colour.

An exponential form fits the UV tailing well and corresponds to 0.66 eV, for the "Urbach" energy, that characterizes the smearing of energy levels within the electronic transition corresponding to the main ultraviolet absorption. Apparently, this energy parameter does not change with exposure in this material, but the increase in tailing may be better accounted for by the transition gap being reduced slightly as degradation continues. The approach of Tauc *et al.* may be useful as a quantification of the spreading of the larger UV peaks centred around 242 nm and 210 nm.

Effective dosage absorbed by the polyester-urethane coating accelerated as the coating degraded, similar to a "positive feedback" response. The form of the acceleration lends itself to some choices that could be used to define the lifetime of the coating. Either one could choose a point at which the adsorbed dosage accelerates noticeably, or one could extrapolate to a point when the dosage has increased vastly. If the causes for the non-linearity in dosage response of a polymer as it changes due to degradation can be understood, then a prediction of service lifetime is brought closer to realisation.

Depending on the choice of quantum yield function, effective dosage calculations demonstrate that different candidates for the source of ultraviolet radiation in accelerated exposure change the relative importance of the features in the absorption spectrum of the polymer. A Xenon arc lamp, filtered through borosilicate glass, more closely matched terrestrial sunlight than a fluorescent source.

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