Chapter 2
Laboratory-Based Predictions of Weathering in Outdoor Environments over the Entire Degradation Pathway

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Abstract A useful estimate of outdoor service life for a material or product based on laboratory weathering experiments requires a careful assessment of the degradation pathways that result from exposure. Furthermore, converting real-world conditions into parameters that serve as inputs to models based on the accelerated weathering stresses of radiation, heat, and moisture is not trivial. In an effort to study these relationships, a model material was weathered under accelerated conditions in the laboratory, from which mathematical formulas were derived to describe the resultant photodegradation rate as a function of irradiance and temperature. Calculations for a specific geographical location yielded degradation as a function of time that exhibited excellent agreement with actual outdoor weathering results over the entire degradation period. Variations on the method of calculation proved the mathematical model to be robust. Investigation of chemical degradation in the model material revealed the possibility of more than one reaction pathway. Such behavior is readily apparent in other polymer systems we have studied, wherein the exposure conditions employed can lead to a lack of synchronization of changes in the material or can produce significantly different degradation pathways, both of which affect lifetime estimates.

Introduction

The objective of a service-life prediction (SLP) protocol is to provide the tools for estimating the functional life of a product without having to wait to measure time to failure in time-consuming, natural weathering tests. SLP can also be employed to

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assess how service life varies when a product is used in different climates or environments. Ideally, the output of an SLP study would be a formula describing the degradation of product function over the course of its lifetime:

$$P(t) = P(0) + \int_0^t \frac{dP}{d\tau} d\tau \qquad (2.1)$$

Here, P is a property that changes over time due to weathering exposure until it reaches a point determined to be indicative of product failure. The rate of this degradation process, $dP/d\tau$, depends on the stresses to which the product is exposed. Generally, the SLP protocol limits these stresses to radiation, heat, and water—those of primary importance in the outdoor environment. The degradation rate also depends on the chemical and physical reactions involved and their associated kinetics, keeping in mind that they may not be zero order. This "degradation-rate" approach is different from accelerated life testing, which instead determines the effect of environmental stresses on time-to-failure data. In so doing, it focuses on the end state of the material. Not only does the degradation-rate method shown here provide time-to-failure estimates; it tracks degradation in the material along the entire pathway to failure.

The value of any SLP approach lies in its ability to predict real-world results. For example, it should be able to provide an estimate of time to failure for a given outdoor location with some degree of accuracy. It should demonstrate that both the manner of degradation and the associated pathway toward failure are identical in the laboratory and outdoor weathering exposures. Finally, it should be able to do this using readily available climate data from multiple global locations as inputs to the stress-dependent formula, such as the degradation-rate model given by Eq. (2.1).

A number of studies have been conducted to investigate how well SLP accomplishes these goals for selected polymer-based materials [1–4]. From these, reasonable estimates of lifetime were obtained as compared to actual values of time to failure observed for outdoor exposures. Some of the predictions covered the entire degradation pathway, for which changes in material properties generally followed a trend similar to that measured during outdoor weathering. The SLP methods employed varied somewhat from study to study and all used measured climate data to test their models.

In order for SLP to continue to gain credibility as a viable tool for gauging the durability of a polymeric material, a careful examination of its capability should be conducted. By performing the investigation with a model material whose degradation attributes are well behaved and generally understood, the SLP protocol itself can be tested. The objectives of the study include:

1. To develop a laboratory-based weathering degradation model and examine it as applied to a real material in a real environment
2. To determine if the model is consistent with the actual degradation rate observed for the material as well as the chemistry and physics responsible for degradation in the material

3. To validate the result predicted by the model over the entire degradation pathway by comparing it with results from a real-world exposure
4. To examine the many approximations made throughout the entire SLP process and assess how robust—and ultimately, how useful—the model will be

One of the advantages offered by this study is the ability to examine the sensitivity of the SLP estimate to climate data. In order to use the SLP model, one must have access to a dataset that includes values for solar irradiance, ambient temperature, and some measure of exposure to water. Since each SLP estimate is particular to a given location in the world, these values generally come from climatic models that are based on multi-year averages. Because weather data will vary from year to year, an assessment of how well these averages represent the weather in any given year is of interest. This study compares SLP results obtained using average climate data with results obtained using weather data measured during the actual outdoor exposure.

A significant challenge encountered in the utilization of the SLP methodology is the need to convert climate data into a form that can be used by the model. For example, solar irradiance for a given outdoor location is typically reported for the wavelength range 290–3,000 nm, but the SLP model is typically based on an irradiance that is experimentally controlled at 340 nm. There are multiple ways to perform the necessary transformations, which could lead to differences in the resulting lifetime estimates. The robustness of the SLP model with regard to these transformations is examined in this study in an effort to assess the level of variability that may result due to the particular transformation selected.

There is also more than one way to apply an SLP model in order to generate a lifetime estimate. Some studies have employed a cumulative damage model in which, akin to the method of Miner's Rule [5], the "fraction of life lost" during each time interval in the exposure is determined and the fractions are summed over all intervals until the point in time at which service life runs out. Others have modeled as a continuous function of time the degradation of a property that relates to the failure mode. This latter method, which has been discussed in the literature in detail [6], served as the basis in this study for determining the complete degradation curve resulting from exposure. The lifetime estimate that it produced is compared herein to a corresponding estimate obtained using the cumulative damage model.

Experiment

The model material that was weathered in this study was a fluorescent yellow poly(vinyl chloride) (PVC) film containing the dye C. I. Solvent Yellow 98, additives typically found in plasticized vinyl, and a hydroxybenzophenone UV absorber. The glass transition temperature (T_g) of the film was below −20 °C, as determined by differential scanning calorimetry. Its transparency, which was retained during weathering, made it possible to conduct a highly quantitative study. The dye fades

Fig. 2.1 Degradation of
absorbance for Solvent
Yellow 98 in polycarbonate
(PC) and poly(vinylchloride)
(PVC) films exposed in
ASTM G155 Cycle 1
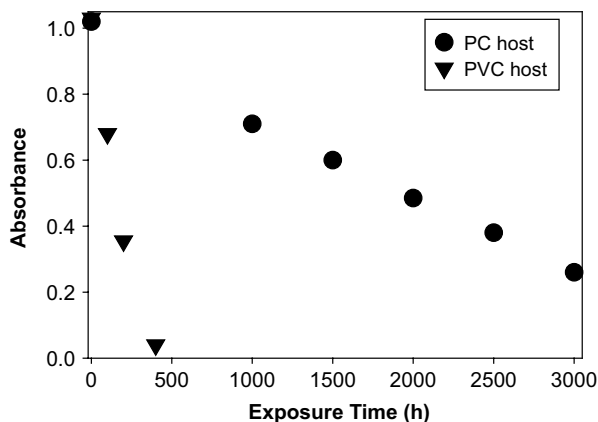
under exposure to light, and the resulting decrease in dye concentration was
monitored via visible absorption spectroscopy.

Although the degradation of interest pertains to dye molecules, the polymer
host has a very significant effect on the rate of degradation of this colorant. Its
lifetime in polycarbonate far exceeds that in vinyl (see Fig. 2.1)[1], thus affecting the
applications for which it can be used in products. Guest-host interactions such as
this are not unusual. The type of guest colorant can also affect the durability of a
polymer host. Regardless, the choice of this model material meets the requirement
of an easily interpretable failure mode that can be used to test the attributes of the
SLP method.

Individual 250-μm film specimens were cut to just over 25 mm × 25 mm in size
and mounted between aluminum plates having 25 mm × 25 mm windows. Prior to
cutting the specimens, the film was annealed at 70 °C for 24 h so that the weathering
exposure itself would not induce any shrinkage that could cause a change in absor-
bance and confound the results. For the outdoor weathering (Arizona45S), the alu-
minum plates containing the specimens were affixed to larger holders (2 specimens
per holder) and mounted unbacked at 45° tilt, facing south at the DSET Laboratories
test site near New River, Arizona. The exposure was conducted according to ASTM
G7-05[2] under direct sunlight from July 23 to October 21, 2008. One holder was
removed from exposure every 5 days up to a total of 30 days and every 10 days
thereafter up to a total of 90 days. For the duration of the test, solar irradiance and
temperature data were collected at 1-min intervals. The irradiance data included
total solar (full spectrum) and TUVR (295–385 nm) measurements made at a 45°
tilt. The temperature data comprised black panel and white panel measurements—
also at 45° tilt—as well as ambient temperatures.

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[1] Exposure conducted according to Cycle 1 in ASTM G155-05a Standard Practice for operating
xenon arc light apparatus for exposure of nonmetallic materials

[2] ASTM G7-05 Standard Practice for atmospheric environmental exposure testing of nonmetallic
materials

The accelerated laboratory weathering was performed in Atlas Ci5000 Weather-Ometers®, each with a xenon arc light source surrounded by a quartz inner filter and a 3M proprietary outer filter [7] to approximate daylight. The weathering cycle consisted of an 8-h segment with light only, followed by a 4-h dark segment, a portion of which included water spray. The experiments employed four different levels of irradiance (0.3, 0.5, 0.75, and 1.0 W/m^2/nm at 340 nm) with white panel temperature (WPT) held at 70 °C and five different levels of temperature (50, 55, 60, 65, and 70 °C) with irradiance held at 0.75 W/m^2/nm. The exposures were temporarily interrupted at regular intervals in order to measure the progress of the specimen degradation. In a separate set of experiments, the effect of exposure to multiple levels of water was also examined. The impact of increasing time of wetness from 4 up to 50 % of total cycle time was found to be sufficiently small that it could be ignored.

Degradation due to weathering was followed by measuring the absorbance of the dyed film as a function of time of exposure. Spectra were measured using a Shimadzu UV-2550 spectrophotometer (UV-2401 for some replicates) set at 1-nm bandpass and equipped with a holder assembly that ensured repeatable positioning of a specimen each time it was measured. A file specimen that was kept in the dark at room temperature was also measured at each interval. Its spectra revealed that the repeatability of the absorption measurement was very near to the photometric repeatability specified for the spectrophotometer (±0.001 absorbance units).

For each spectrum, the peak absorbance at 455 nm was determined. This value was corrected for losses in the spectrophotometer due to reflection at both film surfaces by subtracting the absorbance reading obtained at 800 nm, where no dye absorption was detected. The observed losses were in agreement with reflectivity values predicted from the refractive index of PVC. The peak absorbance was also corrected by subtracting the residual absorbance that persisted at 455 nm after the film had been completely bleached. This method of correcting for residual absorbance gave the same result as scaling the initial absorption band to fit each subsequent one and determining the fraction lost as a function of time. No evidence for weathering-induced yellowing of the PVC host itself was observed.

Results and Discussion

A major premise of SLP, as with any accelerated weathering protocol, is that the degradation pathway resulting when environmental conditions are employed to accelerate the degradation to failure in the laboratory must be identical to the pathway observed for the natural exposure. To verify this condition, absorption spectra for the fluorescent vinyl films measured as a function of weathering exposure are displayed in Fig. 2.2. One can readily see that changes to the spectra followed the same pathway for both the laboratory and outdoor exposures shown. Similar results were observed for the remaining laboratory weathering cycles, thus satisfying the requirement.
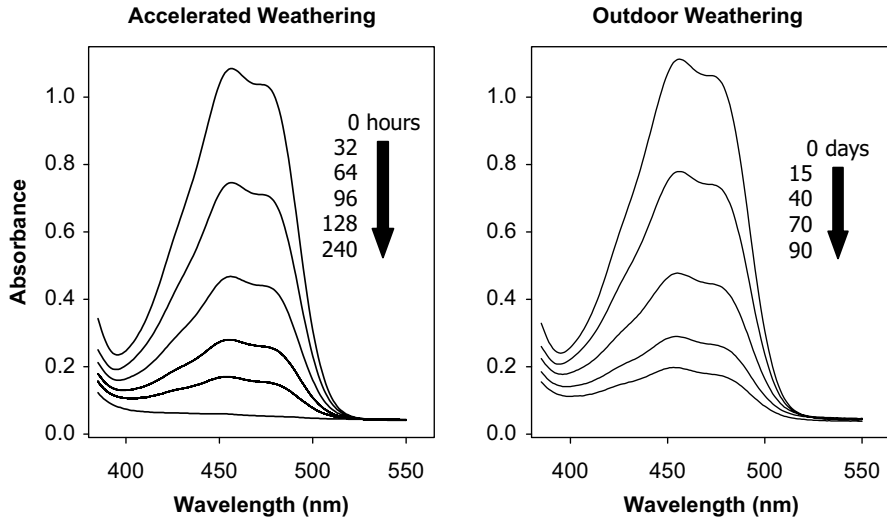
Fig. 2.2 Degradation of absorbance in the fluorescent yellow vinyl films resulting from exposures in the laboratory (I=1.0 W/m²/nm at 340 nm, WPT=70 °C) and outdoors (Arizona45S). These spectra were not corrected for reflection losses

Deriving the SLP Model

In a previous study [8], a model based on a first-order rate equation was derived to account for the effect of irradiance on the degradation rate of dye concentration in the fluorescent vinyl film. This model was subsequently modified to account for the impact of temperature by including an Arrhenius factor:

$$-\frac{dD(z,t)}{dt} = \frac{\sigma^* I(z,t)}{k_2 \sigma^* I(z,t) + k_3} e^{-K\left(\frac{1}{T+273.15} - \frac{1}{343.15}\right)} D(z,t) \qquad (2.2)$$

where D is the local concentration of the dye and I is the local irradiance, both of which depend on depth in the film (z) and exposure time (t). The absorption cross section is given by σ^*. The Arrhenius factor is shown explicitly with fitting parameter K equal to E_a/R, where E_a is the Arrhenius activation energy and R is the gas constant. The effect of temperature T (in °C) is relative to 343.15 K (70 °C), which is used as the reference temperature since the exposures as a function of irradiance all operated at this WPT. Parameters k_2 and k_3 are constants that come from the derivation of the model [8]. Equation (2.2) can express the decrease in absorbance of the fluorescent vinyl films with weathering exposure because dye concentration was determined to be directly proportional to absorbance, in accordance with Beer's Law.

In order to determine the values for K, k_2, and k_3 in the SLP model, the absorbance data obtained as a function of exposure time for all eight laboratory weathering
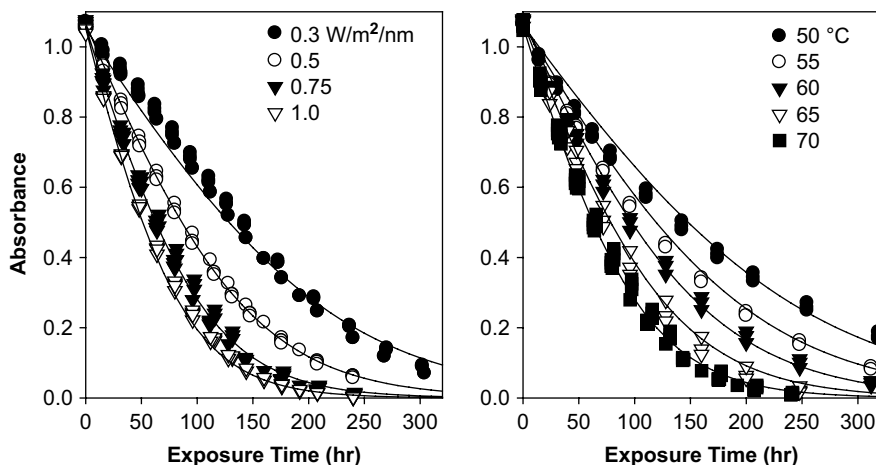
Fig. 2.3 Degradation of peak absorbance in the film specimens as a function of the indicated exposure conditions. The curves represent a simultaneous fit to all of the data using Eq. (2.2)

conditions were fit simultaneously using a simplex algorithm [9] applied to an iterative numerical method described previously [10]. For the experimental absorbance data, exposure time was defined as time during which the light in the weathering chamber was on, since the model predicts no degradation when $I=0$. The fit, represented by the solid curves displayed in Fig. 2.3, yielded K = 4,710 K, $k_2 = 21.0$ s^{-1}, and $k_3 = 53.6$ s^{-2}. Absorbance data for all 33 film specimens included in the study are also plotted in the figure, indicating how well the model accounts for the experimental results.

Individual fits to the absorbance data were also performed for each film specimen according to the conditions under which it was weathered. Defining a pseudo-rate constant, k_{eff}, as the pre-factor of D on the right-hand side of Eq. (2.2), a value of k_{eff} was then determined for each specimen. These values are graphed in Fig. 2.4, showing both the dependence as a function of irradiance and as a function of temperature. The solid curves in the plots were calculated using the aforementioned parameters obtained from the fit of all of the experimental absorbance data. Thus, the curve in the plot of irradiance dependence is also influenced by results from the temperature-dependent experiments, and vice versa. The linear response in the temperature plot signifies Arrhenius-like behavior in the temperature range shown. The lack of linearity in the irradiance plot is indicative of reciprocity failure. The dependence on irradiance given by the model in Eq. (2.2) is different from the commonly used power law. It has been shown [8] to be consistent with photophysics of degradation from the triplet state, previously observed in other dyes of a similar class [11]. An outcome of this expression is that unlike the power law, it exhibits linear dependence at low levels of irradiance, which would be expected in a photochemical reaction.
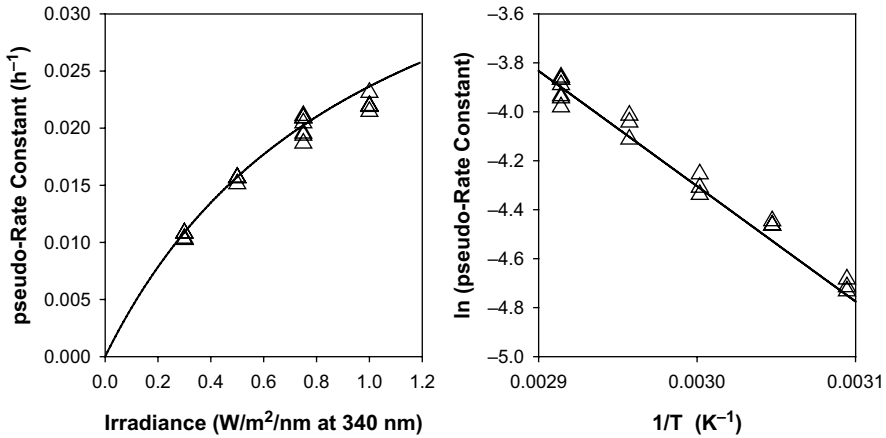
Fig. 2.4 Rate of degradation of absorbance determined for the individual film specimens plotted according to their exposure conditions. The curves were calculated using the parameters obtained by simultaneously fitting all of the absorbance data with Eq. (2.2)

Calculating the SLP Estimate

In order to utilize the derived model to predict degradation of absorbance in the fluorescent vinyl film due to outdoor exposure in Arizona, climate data for the appropriate time period needs to be transformed into a set of parameters that the model can use. With regard to the irradiance parameter, solar irradiance from the outdoor exposure must be represented by an appropriate value for the xenon arc irradiance at 340 nm in the laboratory exposure. Both total solar irradiance (290–3,000 nm) and ultraviolet solar irradiance (295–385 nm, commonly referred to as TUVR) data from the outdoor site were measured during the Arizona45S exposure. However, the graph in Fig. 2.5 shows why a conversion is difficult. The plots of the ratio of total solar irradiance to TUVR measured as a function of time of the day near New River, AZ, for a south-facing, 45° specimen tilt on July 28, 2008, and October 21, 2008, reveal that the fraction of TUVR (and thus, 340-nm radiation) in the total solar irradiance varies significantly with the time of the day and the day of the year. In midsummer, the solar radiation reaching the specimen around dawn and dusk is largely due to light scattering, which favors short wavelength (UV) radiation. Thus, the ratio drops off at the beginning and end of the day. In contrast, during the fall, the solar radiation striking the specimen around dawn and dusk is primarily from direct sunlight, which is deficient in UV radiation that has been scattered out of the light path from the low-lying sun. This causes the ratio to rise sharply. During the middle of the day, when irradiance has its greatest effect on photodegradation, the ratio is fairly constant.

Since TUVR data from the outdoor exposure site were available, it was decided to convert the TUVR to actinic irradiance and then use the measured spectral power
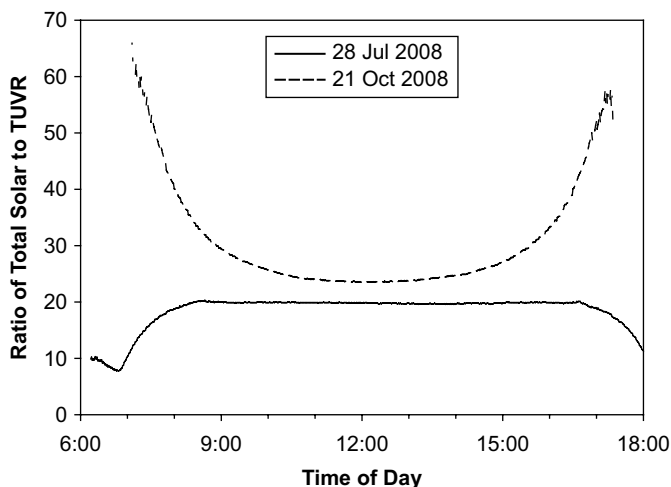
Fig. 2.5 Effect of time of the day and day of the year on the amount of UV radiation present in the total solar irradiance measured at New River, Arizona

Table 2.1 Calculated ratio of irradiance at 400–520 nm to TUVR (295–385 nm) for a specimen near New River, Arizona, facing south, tilted at 45°

Date	Time (approx.)	400–520 nm/TUVR
July 24, 2008	12:30PM	4.1
July 24, 2008	5:50PM	4.0
Sep 6, 2008	12:30PM	4.3
Sep 6, 2008	5:20PM	5.1
Oct 21, 2008	12:00PM	4.8
Oct 21, 2008	4:50PM	7.0

distribution of the xenon arc source to further convert to irradiance at 340 nm for input to the model. It was assumed that the actinic radiation was limited to the 400–520 nm range, since the dye absorbs very strongly in this region compared to the UV, and inclusion of UV absorbers in the film minimized the level of UV radiation reaching the dye anyway. Factors to convert TUVR to actinic irradiance were determined using SMARTS 2.9.5 [12, 13]. The SMARTS calculations provided spectral solar irradiance at a specified zenith and azimuth of the sun for a given specimen orientation and geographical location. The results corresponding to the sun's position near peak solar height and prior to sunset for various days during the Arizona45S exposure are displayed in Table 2.1. The ratios of irradiance at 400–520 nm to TUVR for peak sun were similar throughout the exposure. Closer to sunset the ratios varied to a greater extent, especially in the latter half of the exposure, but under these circumstances, the solar irradiance was significantly lower and had less impact on degradation. Ultimately, a value of 4.1 was selected and adjusted using the spectrum of the xenon arc source to yield a conversion factor set at 0.0154. Irradiance values at 340 nm were determined for the SLP model of the Arizona45S exposure by multiplying measured TUVR data by this constant factor.
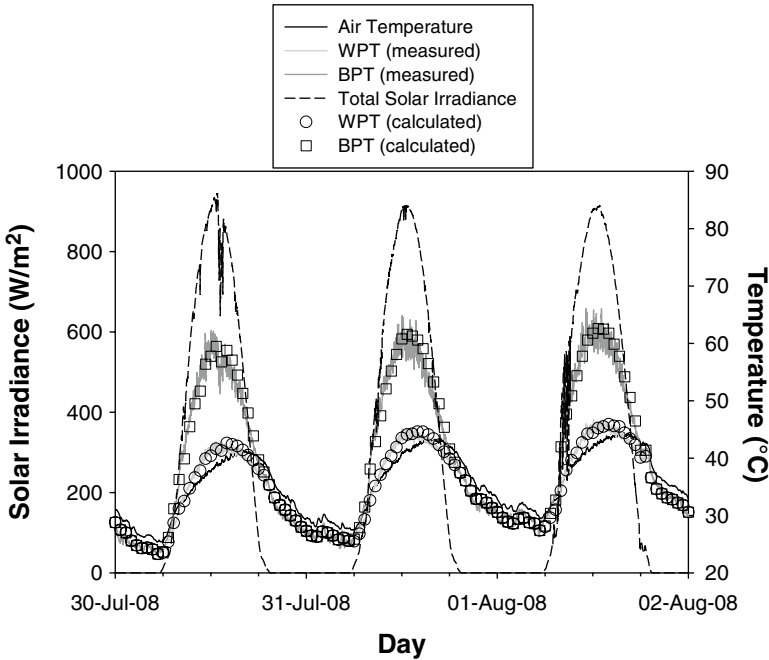
Fig. 2.6 Climate data measured at the exposure site near New River, Arizona. The individual points for WPT and BPT were calculated based on the measured air temperature (in K) and solar irradiance (in W/m²), using the following values for the parameters in Eq. (2.4): $h = 35$ W/m²/K, $\alpha = 1 \times 10^{-8}$ W/m²/K⁴, $\beta = 1 \times 10^{-7}$ W/m²/K⁴, $a = 0.95$ (BPT), and $a = 0.22$ (WPT)

Correlating a temperature that is available from climate data with the WPT parameter that was used to fit the laboratory degradation data by means of the SLP model also poses a number of challenges. Typically, climate data include only ambient (air) temperatures. These must somehow be converted to the WPTs used to control the laboratory weathering devices. Even then, one must consider whether such a conversion would translate to equivalent film specimen temperatures for both the outdoor and laboratory exposures. If the resulting film specimen temperatures are different, the correlation between outdoor air temperature and WPT in a laboratory weathering chamber may not be sufficient to provide a useful SLP estimate.

The relationship between air temperature and a specimen temperature in an outdoor exposure has often been expressed as

$$T_{\text{specimen}} = T_{\text{air}} + \frac{a}{h} I \tag{2.3}$$

where a is the absorptivity for solar radiation by the specimen, h is the combined convection and radiation heat transfer coefficient of the specimen, and I is the total solar irradiance. There is a problem with this expression, however, as demonstrated by the data graphed in Fig. 2.6. If the white panel in the outdoor exposure of Fig. 2.6

is taken to be a specimen, one can readily see from Eq. (2.3) that there is no constant *a/h* factor that could convert the air temperature to the WPT for all points in time. This is because the WPT is sometimes *below* the air temperature, which Eq. (2.3) cannot predict. In fact, Eq. (2.3) was derived as a fictitious "sol-air temperature" for use in determining the effect of solar radiation on heat transfer through buildings [14].

By explicitly accounting for the effect of radiative heat transfer between the specimen and the sky [15], another expression was derived:

$$T_{\text{specimen}} = T_{\text{air}} + \frac{aI - \alpha T_{\text{air}}^4}{h + \beta T_{\text{air}}^3} \tag{2.4}$$

where α and β are parameters that depend on the emissivity of the specimen and its environment. Taking values for air temperature and total solar irradiance plotted in Fig. 2.6, the corresponding WPT can be modeled by Eq. (2.4) using reasonable values for the other parameters. The results depicted in the figure indicate that a good fit can be attained not only for a white panel, but also for a black panel. Nevertheless, for the SLP analysis in this study, it was not necessary to make use of Eq. (2.4). Since white panel (45° tilt, south-facing) temperature data were measured during the Arizona45S exposure, they were used directly in the SLP model for the temperature parameter.

Comparing the SLP Estimate to the Arizona45S Exposure

The SLP model determined via laboratory weathering experiments was employed to predict the degradation of peak absorbance for the fluorescent vinyl film weathered in the Arizona45S exposure from July 23 to October 21, 2008. The resulting prediction, calculated at 1-min intervals, is plotted in Fig. 2.7. The zigzag appearance in the curve comes from the fact that the SLP model predicts no degradation at
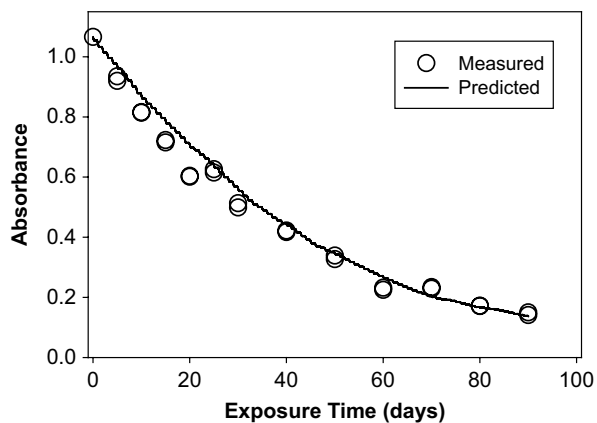

Fig. 2.7 Degradation of peak absorbance in the film specimens predicted by the SLP model for the outdoor exposure near New River, Arizona, from July 23 to Oct 21, 2008. The prediction was based on climate data measured at the site during the exposure. The degradation observed experimentally is shown for comparison

night. The absorbance measured from the fluorescent vinyl film specimens weathered outdoors according to Arizona45S during this same time period is also plotted in the figure. The SLP estimate exhibits excellent agreement with the measured degradation, confirming the validity of the SLP methodology when applied to this material, which degrades relatively quickly due to stresses from solar radiation and heat.

Full exploitation of the SLP model demands the ability to make lifetime estimates for specimens in other orientations and geographic locations. Obviously, measured climate data will usually not be available to make such lifetime estimates. Instead, calculated climate data using models based on averages over many years must be used. One such model, METEONORM, provides hourly data for total solar irradiance and air temperature in numerous locations around the world [16]. Since TUVR and WPT data are not provided, conversions for total solar irradiance and air temperature to the laboratory weathering device parameters of irradiance at 340 nm and WPT, respectively, must be derived.

A SMARTS calculation of solar irradiance around noon near New River, Arizona, for a south-facing specimen at 45° tilt showed that the ratios of 340-nm irradiance to the irradiance from 400 to 520 nm on July 24, September 6, and October 21 were similar to each other (within ±10 %) and to the ratio measured from a xenon arc source used in an SLP weathering device. This means that for a given irradiance at 340 nm, the irradiance for 400–520 nm would be nearly the same in both the Arizona outdoor and laboratory SLP exposures. Therefore, results from the SMARTS calculation were used to assign a value of 0.18 to convert total solar irradiance from METEONORM (in MJ/m^2 for a 1-h interval) to irradiance at 340 nm (in W/m^2/nm) for the SLP model. The true value of this conversion factor actually varies substantially, depending on the day of the year and time of the day. The effect of variability was minimized by selecting a value representative of noontime conditions, when the effect of solar irradiance on the degradation would be greatest.

In spite of the limitations of Eq. (2.3) pointed out previously, it is the simplest expression available to convert air temperature for use in the SLP model. By setting the factor a/h equal to 2, the effects of air temperature (°C) and total solar irradiance (in MJ/m^2 for a 1-h interval) from METEONORM were combined to estimate WPT ($T_{specimen}$ in Eq. (2.3)) for the environmental conditions during the Arizona45S exposure. These calculated outdoor WPTs were used for the WPTs utilized by the SLP model, again making the assumption that this would constitute equal film temperatures in the outdoor and laboratory exposures.

With a means to convert the irradiance and temperature data from METEONORM in hand, values corresponding to Phoenix, Arizona (35 mi/56 km south of New River), for the period July 23 through October 21 were determined and put into the SLP model to generate an estimate for the degradation of peak absorbance in the fluorescent vinyl film exposed under Arizona45S conditions. The predicted absorbance, calculated at 1-h intervals, is plotted in Fig. 2.8 along with the prediction obtained previously using actual climate data measured at the New River site during

Fig. 2.8 A comparison of degradation in the film specimens predicted by the SLP model based on measured and modeled climate data
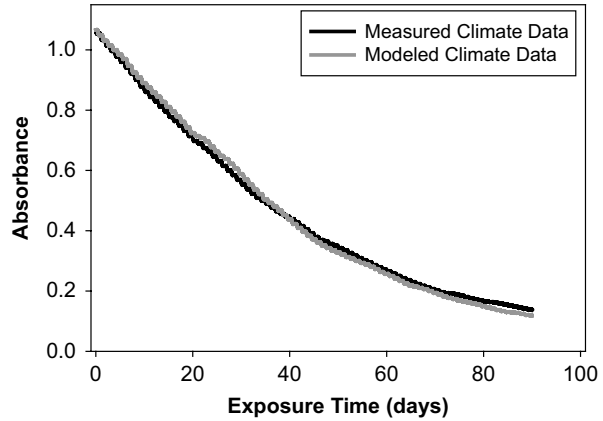
the period of the exposure. The agreement between the two curves is very good, considering the assumptions and approximations that were made to derive the irradiance and temperature data used for inputs to the SLP model.

Comparing the SLP Estimate to Estimates from Alternative Models

Derivation of the SLP model in this study was accomplished via a simultaneous fit of the complete set of absorbance degradation data from the film specimens in all eight SLP exposure conditions. For comparison, we analyzed the experimental data with the cumulative damage model used in accelerated life testing. In this case, lifetime was estimated based on the end state of the degraded material instead of accounting for the entire degradation pathway. Time to failure (t_F) was determined for each of the 33 film specimens exposed in the SLP weathering cycles by interpolating to the point in time at which peak absorbance reached a value of 0.2, an arbitrarily defined failure. All of the t_F values were simultaneously fit with the Accelerated Life Testing module in Minitab® software [17] using the expression

$$\ln t_F = \beta_0 + \beta_1 \ln I + \beta_2 \frac{1}{T} + \sigma\epsilon \qquad (2.5)$$

Table 2.2 A comparison of t_F estimates for failure in fluorescent vinyl film when peak absorbance falls to a value of 0.2. The values were derived from multiple SLP models using two different sources of climate data

SLP model	Climate data	Time to failure (days)
Degradation rate (Eq. 2.2)	Measured	71
Degradation rate (Eq. 2.2)	Modeled	69
Accelerated life test (Eq. 2.5) (sum over fraction of life lost until failure)	Modeled	70
Accelerated life test (Eq. 2.5) (calculated using values for I_{eff} and T_{eff})	Measured	72 ± 7
Outdoor result	Actual	~75

where I is irradiance, T is temperature, and the last term accounts for statistical variability. For the fit, values for I and T corresponded to the irradiance and WPT set points, respectively. The coefficients obtained from the fit ($\beta_0 = -9.26$, $\beta_1 = -0.690$, $\beta_2 = 4,760$) are an indication of the relative effect of these stresses on the degradation.

Using Eq. (2.5), the fraction of life lost could be calculated for a given outdoor exposure interval and the fractions summed over the course of the exposure until failure was reached. As in the previous analysis, I and T were derived from modeled climate data. This yielded the time to failure, displayed in Table 2.2. It is compared with values for t_F determined from each of the degradation curves shown in Fig. 2.8. Following a previously described formalism for deriving constant effective temperature [18], a value for T_{eff} was determined for the accelerated life test model using measured climate data. The formalism was extended to also derive an analog for constant effective irradiance, I_{eff}. These inputs were then used in Eq. (2.5) to calculate t_F. Because constant parameters were used, the calculation enabled an estimation of the error (95 % confidence interval) as well. This is a measure of how well the model fit the experimental data. It does not take into account variability in the climate itself. Even so, based on the value calculated for the error, all of the estimates from the several SLP analyses are in agreement with the experimental outdoor result, as seen in Table 2.2.

Robustness of the SLP Model

A key attribute of any predictive model is its robustness. The SLP model can be deemed robust when its output—the lifetime estimate—is not overly sensitive to variations in the model parameters or in the values of the inputs. This attribute can be examined in three ways. First, the SLP estimate plotted in Fig. 2.7 did extremely well in predicting the degradation of absorbance in the fluorescent vinyl film even with the approximations and assumptions made to derive the inputs to the model from measured climate data. Conversion of solar irradiance data to irradiance at

340 nm made use of a constant factor even though its variability over the course of a day and at different times of the year is significant. The assumption that film specimen temperatures in an outdoor exposure and in a laboratory weathering device are nearly equal if their corresponding WPTs are equal is another possible source of error. The risks of such approximations and the need to exercise caution when employing them have been emphasized [2]. Nevertheless, this study has shown that the SLP model can be successful even when assumptions like these are made.

Second, a comparison of the degradation curves in Fig. 2.8 demonstrates that variability in the inputs to the SLP model did not have a significant effect on the resulting lifetime estimates. Not only did the climate data used to generate these curves come from different sources (measured vs. modeled data); the mathematical expressions used to convert the data into useful inputs to the model were also different. A third approach expressed the inputs as effective temperature and irradiance values that were taken to be constant throughout the duration of the SLP analysis. Despite this, essentially the same result was obtained for all sets of climate data.

Finally, the multiple SLP models examined in this work all yielded essentially the same lifetime estimate. The principal model put forth in this study, based on Eqs. (2.1) and (2.2), analyzed the entire absorbance degradation curve of the fluorescent vinyl film. In contrast, analysis via the accelerated life test model [Eq. (2.5)] targeted a single point—the value of t_F at which the absorbance of the film reached 0.2. The fact that these two approaches led to the same result is a consequence of the theoretical prediction that the inverse relationship between rate constant and failure time will hold [19] provided that:

1. The degradation rate depends on the concentration of a species involved in a microscopic reaction, and
2. That reaction is the single reaction primarily responsible for progress toward failure

The existence of this relationship offers the advantage of universality, in that the accelerated life test model can be applied in cases where derivation of a mathematical expression for the degradation of the property of the material under investigation is not straightforward.

Elucidating the Degradation Pathway

The foregoing requirements that determine the applicability of the accelerated life test model to SLP estimation demand an understanding of the degradation pathways involved. Several supplementary experiments were conducted in order to elucidate the pathway(s) corresponding to loss of 455-nm absorbance in the fluorescent yellow vinyl film that served as the model material in this study. In addition to those

already reported [8], these experiments included exposing samples in the weathering chamber continuously, with dark segments of 0, 16, or 20 h every 24-h period, and exposing samples in sealed vials enriched in oxygen. The results led to several observations:

1. Light was required to initiate and perpetuate degradation [8].
2. There was an apparent induction period at low irradiance [8].
3. Intermittent exposures or addition of oxygen slowed degradation. These conditions also produced increased absorption near 400 nm.
4. After exposure, degradation continued in the dark at a slower rate that was highly dependent on temperature.
5. Lower initial dye concentration reduced the degradation rate [8].
6. Addition of radical scavengers slowed degradation [20].

Interpretation of these observations, in conjunction with degradation mechanisms reported for dyes of a similar class [11, 21], generated a number of hypotheses for the manner by which the degradation proceeds:

1. The fluorescent yellow dye degrades via a bimolecular reaction involving semi-reduced radicals formed from the triplet state.
2. Aerobic conditions deactivate the reactive species, yielding H_2O_2.
3. Oxidation of the dye may compete with the primary degradation pathway.

When deprivation of oxygen under accelerated conditions was investigated as a possible cause of reciprocity failure in the irradiance response, it was discovered instead that oxygen actually slowed the degradation. This can lead to a secondary reaction in the dark, involving oxidation of the dye by peroxide that yields a new absorption band near 400 nm [22]. This secondary reaction seemed to play a minor role, as evidenced by the agreement between the accelerated laboratory exposures and the outdoor experiments. However, if the outdoor exposures had initiated in months with lower irradiance and cooler temperatures, one wonders how well the model may have worked, given the possibility of competing degradation reactions.

An example of a polymer film for which understanding the degradation pathways is critical to predicting lifetime was found for poly(ethylene terephthalate) (PET). The issue here pertained to multiple failure modes that did not necessarily relate to a single degradation reaction. PET films weathered in the laboratory according to a high-irradiance version of ASTM G154 Cycle 1[3] exhibited the same increase in absorbance at 330 nm as specimens exposed outdoors in Florida (5° tilt, open, south-facing). The overlay obtained using an appropriate shift factor can be seen in Fig. 2.9. However, the same shift factor did not produce similar agreement for degradation of the haze induced in the film. This lack of synchronization between changes in absorbance and haze suggested that the laboratory weathering test

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[3]ASTM G154-06 Standard Practice for operating fluorescent light apparatus for UV exposure of nonmetallic materials
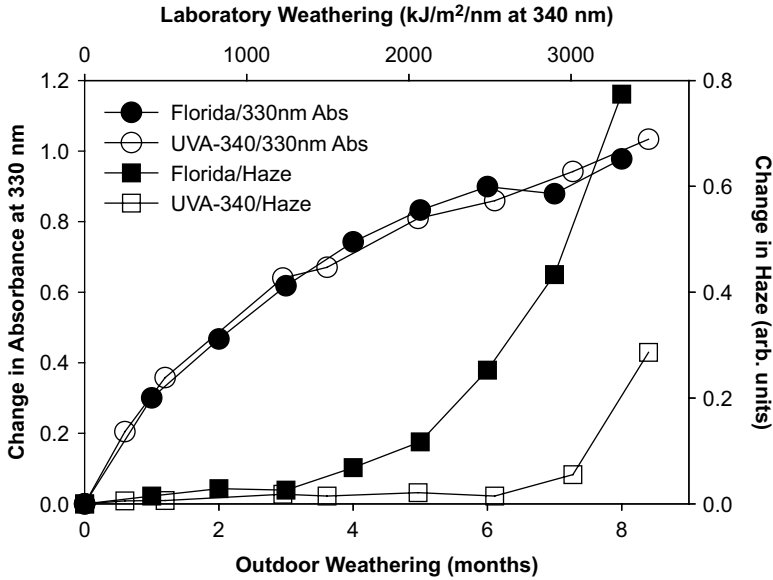
Fig. 2.9 Comparison of the increase in absorbance at 330 nm and haze measured as the average offset in the absorbance spectrum at 580–600 nm for PET films weathered in Florida at 5° tilt and in the laboratory according to ASTM G154 Cycle 1 (UVA-340) at high irradiance. The horizontal axes were scaled relative to each other to give the best overlay for change in absorbance at 330 nm

method did not adequately produce the same degradation in PET as that observed due to outdoor weathering in Florida. After trials with laboratory weathering exposures that included increased cycling of wet/dry periods, it was found that by including a sufficiently long exposure to water and utilizing a xenon arc light source with a full solar spectrum, degradation causing changes in absorbance, haze, and gloss is brought into synchronization (see Fig. 2.10).

Nevertheless, all is not solved. Microscopic observation of the surfaces of the weathered PET films revealed changes in chemistry and micro-cracking due to weathering that were not identical in both the laboratory test method and outdoor exposure. In particular, the FTIR spectrum of the surface of the PET sample exposed in Florida revealed generation of chemical species that were not reproduced via the laboratory test. Even orientation of a sample can affect synchronization of failure modes by altering the relative amounts of solar irradiance and water to which the specimen may be exposed.

Fig. 2.10 Synchronization
of multiple failure modes in
PET films achieved for both
the outdoor Florida and
accelerated xenon arc
weathering exposures
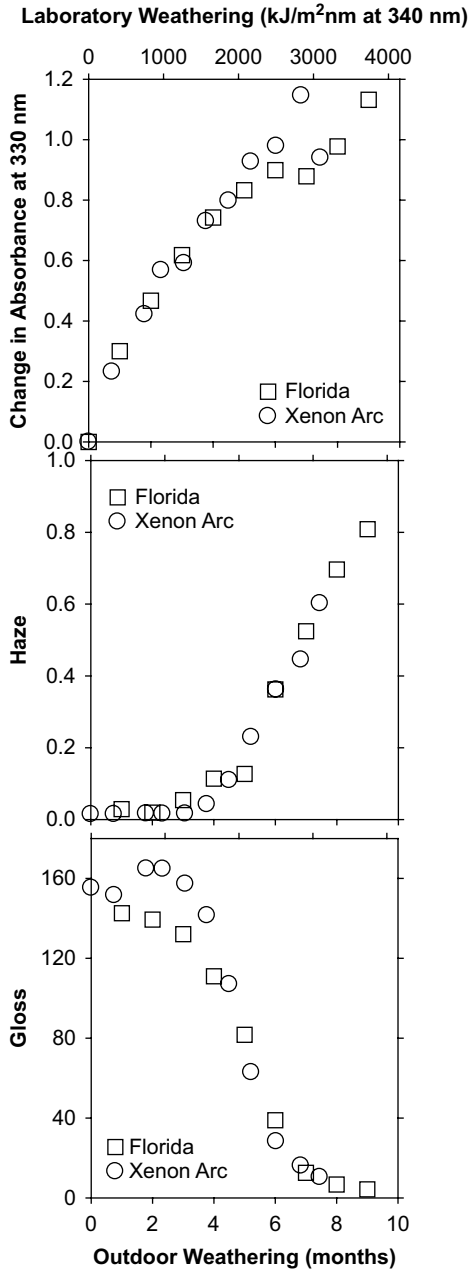
Conclusion

This comparative study has definitively demonstrated an SLP test protocol that can provide a lifetime estimate in excellent agreement with the observed lifetime of a material that degrades in the out-of-doors due to color fade arising primarily from solar radiation and heat. Furthermore, the prediction was shown to be valid for the entire degradation curve of the material and not limited to a single time-to-failure estimate. Seeing that the fluorescent vinyl film that was studied suffered loss of absorbance over a period of only a few months, it is understandable that additional validation studies are needed for more durable materials having other failure modes. Furthermore, the degradation of the fluorescent dye basically followed first-order kinetics. Degradation of other aspects of appearance, mechanical behavior, and physical properties of other polymeric and inorganic materials may not be so easily described and could pose challenges when trying to model change occurring throughout the period of the outdoor exposure.

A significant finding is that the SLP model was determined to be fairly robust. The validity of the model was first affirmed by obtaining input values from climate data measured during the actual exposure period. However, when inputs were derived from modeled climate data for the same time period, the resulting estimate was essentially the same. The utility of SLP estimates has been questioned, given the fact that climatic conditions vary so much from year to year. In this case, using modeled climate data based on 20- and 30-year averages proved to still give a viable prediction of lifetime. Further evidence of robustness was found in the relative insensitivity of the SLP model to the method for conversion of climate data into irradiance and temperature inputs and whether the analysis applied to the full set of degradation data or to time-to-failure values only.

This study has spawned a number of discoveries that will also be useful when analyzing and interpreting SLP data. Extraction of irradiance values at 340 nm from total solar irradiance data should include an evaluation of the impact of time of the day and day of year. Investigating the role of radiative heat transfer in the temperature of a specimen may lead to better modeling, not just for input temperatures for SLP estimates but also for determining temperature distributions in products whose designs may limit allowable temperatures. The degradation mechanism is also very important. If multiple pathways occur or if degradation is not directly dependent on the concentration of a single species, the SLP model may not be suitable for estimating lifetime without appropriate modifications.

The success of this comparison between the SLP estimate and the observed degradation in an outdoor exposure was for a material in which only stresses due to solar radiation and heat were significant. It is well known that water can have a great impact on the degradation and failure of many other materials. Significant progress has been made for some materials in accounting for the effect of relative humidity on time to failure [23]. However, modeling the impact of dew and rainfall poses a challenge, including how to measure them. There is much need for improving the theoretical, experimental, and empirical aspects of the weathering stress that water affords in order to include it in SLP models.

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