Modeling Photodegradation in Transparent Polymers

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ABSTRACT: A model for photodegradation of transparent thermoplastics has been developed and tested using data from polystyrene samples. The proportionality between incident energy and amount of degradation is calculated at each wavelength to yield the "wavelength sensitivity spectrum" for degradation of the polymer. The formal derivation of the wavelength sensitivity spectrum is described. The model was tested by exposing polystyrene samples containing several different stabilizers at various loadings to two different sources of xenon arc ultraviolet radiation. The degradation rates predicted by the model correlated well with the experimentally observed rates over all the different conditions. The model systematically underestimates the absolute degradation. Measurement of stabilizer concentration as a function of depth into the molded test specimens showed that the stabilizer was distributed uniformly before exposure to the light source. After exposure, the stabilizer was largely depleted from the surface layer, but the concentration was unchanged in the bulk of the specimens.

Introduction

Ultraviolet (UV) light constitutes less than 6% of the total energy in sunlight, but it contains the most energetic wavelengths.[1] Photons in the solar UV have sufficient energy to break many common chemical bonds, and these photons are primarily responsible for initiating polymer photo-oxidation. Therefore, for most polymers to achieve useful lifetimes in an outdoor environment, they must be formulated with UV stabilizers to minimize degradation.

Transparent polymers used in outdoor environments are usually stabilized against UV degradation by addition of a UV absorbing additive, which strongly absorbs the damaging wavelengths of light and dissipates the energy harmlessly. The most effective stabilization is accomplished by concentrating the UV absorber in a thin surface layer, which is mainly practiced in extruded sheet applications. For example, in polycarbonate sheet, a cap layer containing a concentrated UV absorber may be coextruded over the bulk sheet to achieved extended weatherability.

Numerous UV absorbers are available, and their stabilizing effectiveness can vary significantly. The effectiveness of these stabilizers is determined empirically by formulating samples and weathering them either outdoors or in an accelerated weathering device such as a xenon arc Weather-Ometer. Because this type of evaluation is time consuming and labor intensive, a model which predicts the weatherability of a transparent polymer with any given UV absorber would be valuable. Such a model should include the power spectrum of the incident light, the wavelength dependence of polymer degradation, the optical absorbance due to one or more UV absorbing stabilizers, and the absorbance of the polymer itself.

This paper develops the mathematical formalism of a weathering model for polystyrene. A modified method of determining the light source-independent wavelength sensitivity spectrum from exposures of specimens behind cutoff filters is presented, and the wavelength sensitivity spectrum is used along with measurements of yellowing for several UV-stabilized polystyrene samples to test the validity of the model. The model formalism can be applied equally well to other unfilled, unpigmented, amorphous polymers.

Background

There have been numerous attempts to model the photodegradation of polymers and the effects of UV-absorbing stabilizers in them. Over 30 years ago, Schmitt and Hirt defined a quantity they termed "protective effectiveness," which quantified stabilizer effectiveness relative to unstabilized polymer.[2] More recently, Pickett examined the effect of thickness of the stabilized zone of the polymer,[3] and Andrady and Shultz investigated the screening of light by pigments and UV absorbers.[4] These methods generally considered the attenuation of energy at a single wavelength in the absorbance spectrum of a UV stabilizer and assumed that the UV stabilizer's absorbance followed Beer's Law. Other workers have developed the concept of polymer wavelength sensitivity spectra and have measured such spectra for a number of important polymers.[5–9]

The model described in this paper represents the combination of the two independent approaches to degradation: single wavelength Beer's Law type models for photodegradation are coupled with polymer wavelength sensitivity information to yield a light source-independent sensitivity spectrum and a model for photodegradation that allows estimates of degradation rates based on simple absorbance measurements.

Wavelength Sensitivity. The relative sensitivity of a photoreaction or sequence of photoprocesses in a polymer expressed as a function of the wavelength of the incident light is termed the "wavelength sensitivity spectrum." The wavelength sensitivity spectrum is influenced by the type of reaction being monitored, the structure of the polymer, and the presence of additives or impurities. In practice, a light source used to determine a wavelength sensitivity spectrum does not provide equal intensity at all wavelengths, and if the data are not corrected for this factor, then the sensitivity spectrum is specific to the light source employed in the measurement.

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Early literature[5] used the term "activation spectrum" to mean a source-dependent wavelength sensitivity spectrum, often derived from exposure of samples to polychromatic radiation. The term "action spectrum" was used synonymously with "wavelength sensitivity" in numerous publications to mean source-independent data. The action spectrum is generally a function describing the dependence of damage per available photon on the wavelength of the radiation, and it derives from experiments using monochromatic radiation, in which both the light energy and damage to the sample are measured. In recent literature the distinction between activation spectra and action spectra has been maintained: monochromatic exposure experiments yield action spectra, and polychromatic light experiments (involving cutoff filters) yield activation spectra. The measurements described in this paper yield information on the sensitivity of the polymer to damage independent of the intensity profile of the light source, yet are derived from exposure of samples to polychromatic radiation. The general term "wavelength sensitivity spectrum" is used.

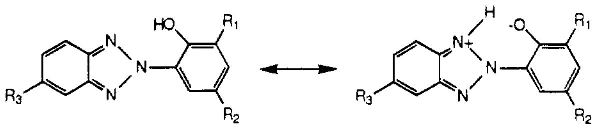
While source-specific activation spectra are useful in certain circumstances, a general, source-independent wavelength sensitivity spectrum is required to build a model of photodegradation that will be applicable to different radiation sources. The general wavelength sensitivity spectrum describes the polymer response as a function of the wavelength of light independent of intensity, and it is intrinsic to the polymer. In the absence of synergism and mutual cancellation effects, the source-specific and source-independent wavelength sensitivity spectra are interconvertible, if the power spectrum of the light source and the dependence of reaction rates on light intensity are known precisely.

In principle, the most direct method of determining a wavelength sensitivity spectrum is to use a source of monochromatic light and measure the polymer response over a range of wavelengths. The source of monochromatic light is typically a xenon arc lamp coupled with a diffraction grating[10-13] or quartz prism[5,6,14] spectrograph. In these experiments, the polychromatic xenon arc light is dispersed into its component wavelengths and projected on a single plastic specimen. The dispersion in these experiments depends on the optical arrangement, but is typically in the range of 20–50 nm per millimeter of sample dimension. Since the entire UV spectrum is dispersed over only a few millimeters of sample, the resolution of the derived wavelength sensitivity spectrum depends on the spatial resolution of the property measurement. Complications with these techniques should be expected for transparent or translucent specimens which reduce wavelength resolution by scattering and internal reflection.

Sharp cutoff Schott glass filters coupled with a polychromatic light source can also be used to determine wavelength dependence.[7-9,15,16] This method has several advantages over the monochromatic light techniques. The filters are inexpensive, and a set of filters covering the wavelength range of interest may be utilized to obtain a simultaneous exposure. Relatively large samples (typically 5 cm × 5 cm) can be used, which means that more precise property measurements can be made. Perhaps the most significant advantage of this technique is that polychromatic light models the actual service exposure of a specimen more closely than does monochromatic light. This fact is important since a variety of processes may occur simultaneously during weathering. These processes, which are often activated by different wavelengths, compete for reactants.[7] By systematically removing the shorter wavelengths from the UV irradiation spectrum, the wavelength sensitivity may be determined using exposure conditions which more closely match the actual exposure.

Stabilization. Hindered amine light stabilizers (HALS) and UV absorbers (UVA) are two classes of stabilizers which are commonly used in transparent polymers. The HALS operate by a free radical scavenging mechanism and they are effective in many polymers, including styrenics and polyolefins. A review of HALS mechanism and performance can be found in ref 17.

UV absorbers function by absorbing strongly the damaging wavelengths of light and dissipating the energy as heat. Benzotriazoles and benzophenones are the two most commonly used types of UVA's, and they both dissipate absorbed energy by undergoing tautomerism, illustrated below for a generic benzotriazole:



The effectiveness of a UVA depends on a number of factors, particularly its absorbance spectrum and concentration in the polymer. It must be evenly distributed in the matrix, which requires that it be compatible with the polymer. In order for a UV absorber to maintain its effectiveness over time, light stability and extraction resistance are also required.

Stabilizer Permanence. A physical loss of UVA can occur by diffusion of the UVA to the polymer surface and subsequent loss through evaporation or physical removal.[18,23] Solubility, volatility, and diffusion coefficients of the UVA are all important to physical loss. Clearly, environmental conditions such as temperature and water or solvent exposure also play a role in UVA loss.

Although UVA's are usually considered to be extremely light stable, losses by photochemical or photooxidative reactions can also occur.[19-21] Rates of UVA degradation depend upon the UVA structure as well as the polymer matrix. For example, polymers with polar groups which can disrupt the internal hydrogen bond of the UVA and those which generate free radicals were found to accelerate the photodegradation of UVA's.[20] This study also showed that the short wavelengths of light are primarily responsible for UVA photodegradation, and the kinetics of the process appear to be zero order.

Derivation of the Model

Assumptions. A useful model for photostabilization of transparent polymers by UV-absorbing stabilizers will include polymer characteristics, such as absorbance spectrum and relative sensitivity to radiation, stabilizer characteristics, such as absorbance spectrum and concentration, incident light source characteristics, specifically the power spectrum, and the geometric characteristics of the sample, such as part thickness or path length of light. The model developed in this paper includes these characteristics in the context of a simple Beer's law absorption of light at each wavelength in the light source spectrum. The sensitivity of the polymer to light of different wavelengths is determined empirically using Schott glass cutoff filters as described below.

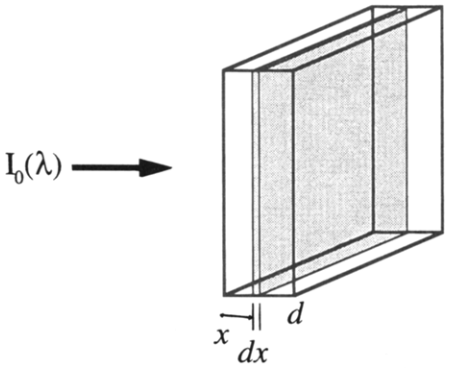


Figure 1. Pictorial representation of polymer sample exposed to incident radiation of irradiance spectrum $I_0(\lambda)$.

A number of simplifying assumptions were made concerning the photodegradation process:

(1) Polymer degradation is linearly proportional to the energy dose of the incident light—and therefore linear in light intensity and in time—regardless of other processes such as diffusion or oxidation.

(2) The wavelength-dependent sensitivity of the polymer toward degradation (its *wavelength sensitivity spectrum*) is invariant over time.

(3) Photostabilizers act only to screen the incident light as absorbers and therefore limit the energy dose received by the polymer.

(4) The absorbance of photostabilizers is governed by Beer's law.

(5) The photostabilizers whose action is being modeled are distributed uniformly throughout the polymer, and their concentration does not change with time. (The effect of other photostabilizers, such as HALS, that change the mechanism of photodegradation, will be reflected in the wavelength sensitivity spectrum.)

The applicability of these assumptions is discussed below in the section comparing experimental degradation rates with predicted rates.

Development of the Model. The assumptions outlined above can be applied to derive an expression for the degradation rate in a specimen of uniform thickness and with uniformly distributed UV stabilizer. This expression can be modified to calculate degradation rates in multilayer systems, where the identity and concentration of UV stabilizers is different from layer to layer, or in systems containing multiple stabilizers.

Model for Uniformly Distributed Stabilizer. Consider a block of polymer of thickness d and unit cross-sectional area which undergoes degradation of some property P when exposed to light of incident irradiance $I_0(\lambda)$ (Figure 1). According to Beer's Law, eq 1, light

$$I = I_0 10^{-A} = I_0 10^{-\epsilon c x} \qquad (1)$$

intensity at some depth x into a sample is attenuated exponentially by the absorbing species in the sample, where I_0 is the incident light intensity, I is the light intensity at distance x into the sample, A is the absorbance, ϵ is the extinction coefficient and c is the concentration of absorbing species.

Using Beer's Law and the assumptions above, the property degradation ΔP of a slice of thickness dx at some distance x into the polymer due to irradiation at wavelength λ will be given by

$$\Delta P(\lambda,x) = E(\lambda,x)S(\lambda) = tI_0(\lambda)10^{-(\Sigma\epsilon_i(\lambda)c_i)x}\,S(\lambda) \qquad (2)$$

where $E(\lambda,x)$ is total energy dose received at wavelength λ and depth x, $S(\lambda)$ is the sensitivity of the polymer to light of wavelength λ (the wavelength sensitivity spectrum), and $\Sigma\epsilon_i(\lambda)c_i$ is the sum of the absorbances of the various absorbing species in the polymer, specifically the polymer itself and any UV-absorbing additives. Assuming that the polymer obeys Beer's Law, the product $\epsilon(\lambda)c$ for the polymer may be replaced by $A(\lambda)/d_p$, where $A(\lambda)$ is the measured absorbance of a polymer sample of thickness d_p. The energy incident upon a sample of unit area is expressed as the light source irradiance, $I_0(\lambda)$, multiplied by the time of exposure t. Integrating from $x = 0$ to d, and dividing both sides by t, we obtain an expression for the rate of photodegradation, eq 3.

$$\frac{\Delta P(\lambda)}{t} = I_0(\lambda)\frac{[1 - 10^{-(\Sigma\epsilon_i(\lambda)c_i)d}]}{\Sigma\epsilon_i(\lambda)c_i}S(\lambda) \qquad (3)$$

The total degradation rate in the polymer is determined by integrating (numerically) over all wavelengths, using experimentally determined source spectra, absorbance spectra, and wavelength sensitivity spectra.

$$\frac{\Delta P}{t} = \int I_0(\lambda)\frac{[1 - 10^{-(\Sigma\epsilon_i(\lambda)c_i)d}]}{\Sigma\epsilon_i(\lambda)c_i}S(\lambda)\mathrm{d}\lambda \qquad (4)$$

If multiple UV stabilizers are present, then the contributions of each are included in the summations of $\epsilon_i(\lambda)c_i$.

Model for Coextruded Sheet. In the case of a structure with a protective "cap" layer, such as coextruded polymer sheet with a cap layer containing a high concentration of UV absorber, the model can be modified to take the multilayer structure into account. The expression for degradation rate of the cap layer is the same as eq 4. Through the thickness of the cap layer, the radiation is attenuated by a factor of $10^{-(\Sigma\epsilon_i(\lambda)c_i)d_0}$, where d_0 is the thickness of the cap layer. This attenuated radiation is incident upon the second layer of the two-layer structure. Thus, the expression for degradation of the total structure is

$$\frac{\Delta P}{t} = \int I_0(\lambda)S(\lambda)\left\{\frac{[1 - 10^{-(\Sigma\epsilon_i(\lambda)c_i)d_0}]}{\Sigma\epsilon_i(\lambda)c_i} + 10^{-(\Sigma\epsilon_i(\lambda)c_i)d_0}\frac{[1 - 10^{-(\Sigma\epsilon_j(\lambda)c_j)(d-d_0)}]}{\Sigma\epsilon_j(\lambda)c_j}\right\}\mathrm{d}\lambda \qquad (5)$$

where the sum over i accounts for the species present in the cap and the sum over j accounts for the species present in the second layer.

Determination of the Wavelength Sensitivity Spectrum. After expressions (4) and (5) are obtained, the problem of predicting degradation rates becomes a problem of obtaining a useful wavelength sensitivity spectrum for the polymer's degradation, $S(\lambda)$. The wavelength sensitivity spectrum must be determined for each polymer under consideration. In general, a separate wavelength sensitivity spectrum should be determined for each degradative property to be modeled, since different processes may be responsible for different types of degradation. If the measured wavelength sensitivity spectra for two different degradative processes, for example, color formation and molecular

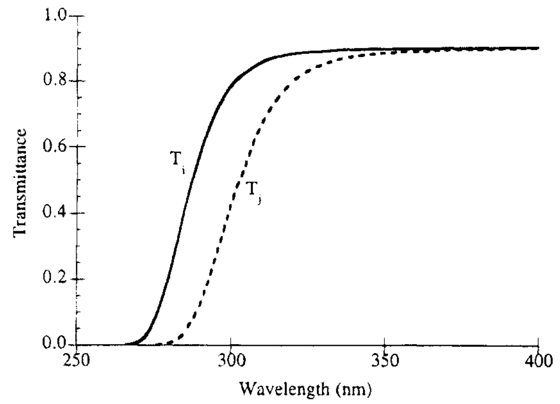


Figure 2. Representative transmission spectra for Schott glass cutoff filters used in the determination of wavelength sensitivity spectra.

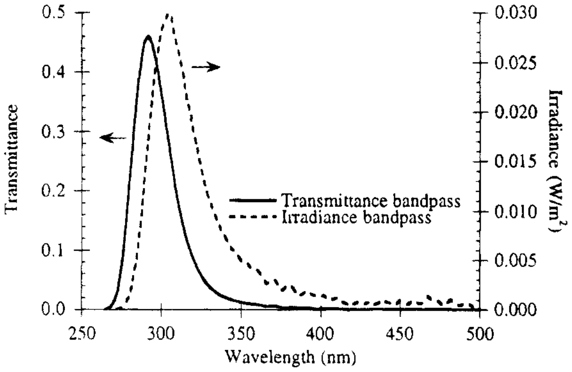


Figure 3. Transmission band pass obtained by subtracting the transmission spectra T_i-T_j of Figure 2 and irradiance bandpass obtained by multiplying transmission bandpass by the light source irradiance spectrum.

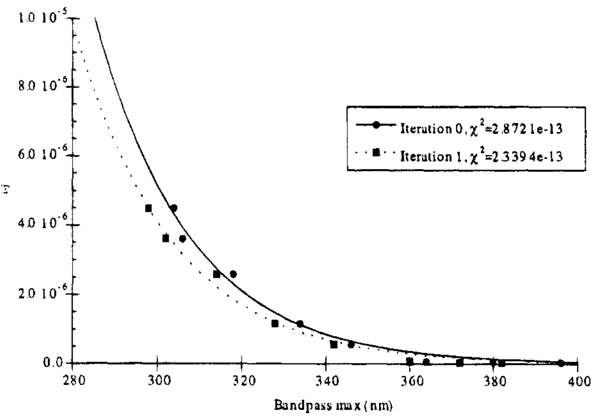


Figure 4. Iteration of wavelength sensitivity spectrum by weighting irradiance bandpasses with trial wavelength sensitivity spectrum. Iteration 0: *S* values plotted against irradiance bandpass maxima. Iteration 1: *S* values plotted against maxima of irradiance bandpasses weighted by curve fit to iteration 0. Convergence occurs after one iteration.

weight loss, are similar, then one may infer that the same or similar processes are rate limiting in both types of degradation.

The wavelength sensitivity spectrum $S(\lambda)$ is determined by exposing unstabilized polymer samples to a radiation source behind sharp cutoff filters. Differences in property degradation between samples exposed behind pairs of different cutoff filters ($\Delta(\Delta P)$) are ascribed to the radiation in the band of wavelengths that is transmitted by one filter but blocked by the other (eq 6). Here, T_i and T_j are the transmission spectra of a pair of cutoff filters.

$$\frac{\Delta(\Delta P)}{t} = \int I_0(\lambda)[T_i(\lambda) - T_j(\lambda)]\frac{[1 - 10^{-(\Sigma\epsilon_i(\lambda)c_i)d}]}{\Sigma\epsilon_i(\lambda)c_i} S(\lambda)\mathrm{d}\lambda \tag{6}$$

Figure 2 shows typical transmission spectra for a pair of Schott glass cutoff filters used in this study. The difference in the transmission spectra results in the transmission "band" plotted in Figure 3. The transmission band is multiplied by the irradiance spectrum of the light source used in the experiment to obtain an "irradiance bandpass". The shape of the irradiance spectrum of the xenon arc lamps used in this study tends to shift the maximum of the irradiance bandpass to longer wavelengths than the transmission bandpass, as shown in Figure 3.

The wavelength sensitivity spectrum is assumed to be constant over this narrow wavelength range of the irradiance bandpass, allowing the value of *S* to be moved outside the integral. The value of *S* over this narrow wavelength range is determined by dividing the measured differential degradation rate, $(\Delta(\Delta P))/t$, by the integrated expression in the denominator of eq 7. The

$$S_{i-j} = \frac{\Delta(\Delta P)}{t\int_\lambda I_0(\lambda)[T_i(\lambda) - T_j(\lambda)]\frac{[1 - 10^{-(\Sigma\epsilon_i(\lambda)c_i)d}]}{\Sigma\epsilon_i(\lambda)c_i}\,\mathrm{d}\lambda} \tag{7}$$

total wavelength sensitivity spectrum can be estimated by using a series of cutoff filters with varying cutoff frequencies in the wavelength range of interest.

The value of *S* for a particular filter pair is assigned to the maximum of the irradiance bandpass for that filter pair. The wavelength sensitivity spectrum can be refined further by recognizing that *S* is not truly constant over the band. An iterative process yields an improved wavelength sensitivity spectrum. First, the *S* values are plotted against the irradiance bandpass maxima as described above. Then, a curve fit is applied to these data points to generate a continuous trial wavelength sensitivity spectrum. For polystyrene, a simple exponential decay function fits the data reasonably well. Each irradiance bandpass is multiplied by the trial wavelength sensitivity spectrum to generate weighted irradiance bandpasses, thereby accounting for the greater sensitivity of the polymer to shorter wavelengths. New bandpass maxima are determined from the weighted irradiance bandpasses and the *S* values are replotted against the new bandpass maxima. An exponential decay curve is fit to the shifted data, and the irradiation bandpasses are re-weighted by the new curve fit. The process is repeated until the weighted bandpass maxima no longer shift. In practice, the wavelength sensitivity spectrum for polystyrene yellowing converged after only one iteration (Figure 4).

Predicted Trends

A number of predictions about degradation rate can be made based on eq 4. An understanding of the functional relationship between degradation rate and such parameters as stabilizer concentration, stabilizer distribution, part thickness, and incident light spectrum can lead to rational design of stabilizer packages appropriate to the desired end performance.

Degradation *vs* Stabilizer Concentration. The assumed Beer's law dependence of stabilizer absorbance on concentration and path length results in predictions of diminished incremental effectiveness of stabilizer.

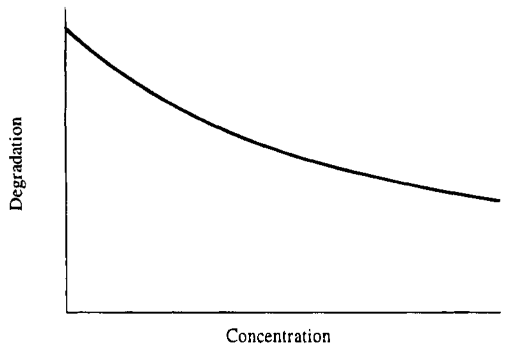


Figure 5. Plot of degradation rate as a function of stabilizer concentration, showing diminished incremental effectiveness of the stabilizer.

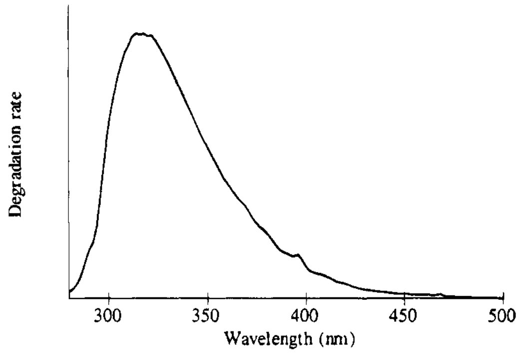


Figure 6. Plot of degradation rate *vs* wavelength for an example stabilized polystyrene, showing those wavelengths causing the greatest damage in the stabilized system. In this example, the calculation is for polystyrene stabilized with 0.02% (w/w) of TINUVIN 571 UV stabilizer and exposed to quartz-borosilicate filtered xenon arc radiation.

Figure 5 shows the trend of degradation rate *vs* stabilizer concentration. At low stabilizer concentrations, the incremental effectiveness of additional stabilizer is large; at large concentrations, the degree of stabilization imparted by additional stabilizer is smaller, approaching an asymptotic limit at very large concentrations.

Degradation *vs.* Thickness. The relationship between degradation rate and part thickness, or path length, is identical to that between degradation rate and stabilizer concentration, since both path length and concentration enter into eq 4 in the same way. Increasing the thickness of a part will increase the total amount of degradation (*e.g.*, yellowing) observed, but the incremental degradation per unit thickness will decrease as the part thickness is increased.

Degradation as a Function of Wavelength. From the model it is possible to compute the damaging effects of radiation *not* attenuated by the photostabilizer in a stabilized system. That is, after filtering certain wavelengths from reaching the polymer, the damaging effects of the remaining transmitted light can be deduced. An example is given in Figure 6. The damage maximum is dependent on the light source as well as the photostabilizer.

This information is unavailable in the absence of the model and could be of use in designing multicomponent stabilizer systems, in which several different stabilizers are used to span the range of damaging wavelengths. For example, one stabilizer could be augmented by adding another which absorbs damaging wavelengths transmitted by the first, potentially resulting in a mixture that is less expensive than increased quantities of a single stabilizer.

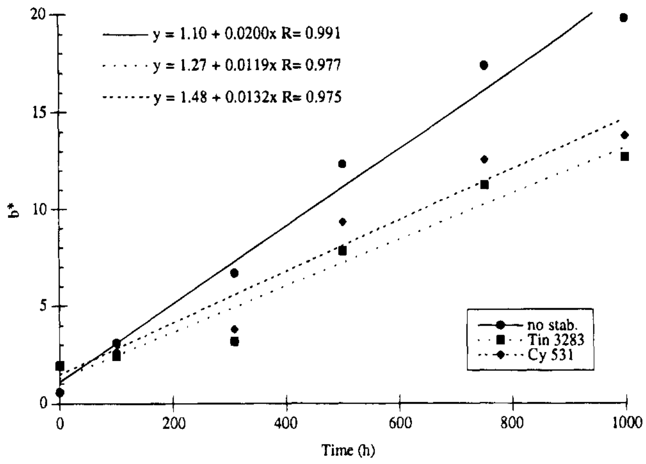


Figure 7. Plot of yellowing *vs* time for three polystyrene samples, showing the linearity of the yellowing rate with time.

Testing the Model Assumptions

A number of simplifying assumptions used in deriving the model were identified above. The appropriateness of the model depends upon how well the assumptions reflect reality.

Linearity of Degradation Rate with Incident Energy. The linearity of degradation with total incident energy, or with time, will depend on the polymer under consideration and the property being modeled. Figure 7 shows the time dependence of development of yellowness in several polystyrene samples as measured by the b^* coordinate on the CIE Lab color scale.[22] In this example, a linear fit through the data points yields lines with correlation coefficients (R) acceptably near unity. However, in all three data sets it appears that the yellowing rate may be decreasing at longer times. This behavior was noted generally for all of the polystyrene samples considered. For the purposes of this model, the yellowing rate was assumed to be constant, while recognizing that this assumption may not be valid at longer times.

Uniformity of Stabilizer Distribution. If the stabilizer is distributed uniformly through the depth of the polymer specimen, then eq 4 will be an appropriate model; however, if the stabilizer migrates or blooms to the polymer–air interface or otherwise becomes nonuniformly distributed through the depth of the sample, then some variant of eq 5 will better represent the system. In general, the uniformity of the stabilizer distribution in a polymer will depend upon the conditions under which the stabilizer is incorporated into the polymer and upon the degree of solubility and the rate of migration of the stabilizer in the polymer. The degree of solubility of the stabilizer will depend upon the chemical structures of the stabilizer and polymer, while the migration rate will depend upon polymer and stabilizer molecular weights and the interactions between the stabilizer and polymer.[23] To assess the uniformity of stabilizer distribution of stabilizer in the molded polystyrene specimens used in this study, the bulk stabilizer concentration was compared with the stabilizer concentration of a 15–20 μm section microtomed from the top of the specimens. The stabilizer concentrations were determined by gel permeation chromatography. The results of the determination are presented in Table 1. No significant differences between the surface and bulk concentration was observed for the samples measured.

Table 1. Comparison of Surface and Bulk Concentrations of UV Stabilizers in Injection-Molded Polystyrene Test Specimens

stabilizer	bulk concn (%)	surface concn (%)
TINUVIN 328	0.022	0.021
TINUVIN 328	0.063	0.063
TINUVIN 328	0.233	0.238
CYASORB 531	0.078	0.123
CYASORB 531	0.085	0.082
CYASORB 531	0.258	0.247

Stabilizer Permanence. The time dependence of the model has been greatly simplified by assuming degradation to be a linear function of time and by assuming that the polymer and stabilizer characteristics (*e.g.*, concentration, absorbance spectrum) do not change with time. These approximations are an oversimplification, at least in the case of constancy of stabilizer concentration and distribution. To investigate the permanence of stabilizers in the polystyrene samples evaluated for this study, the concentration of stabilizer in a sample that had been exposed to quartz-borosilicate filtered xenon arc radiation for 500 h was determined. Measurement of concentration of TINUVIN 328 UV stabilizer by reversed-phase HPLC showed that at least half of the stabilizer was depleted from the top 30 μm of the sample, while the bulk concentration was unchanged (Figure 8). Stabilizer depletion has also been observed in acrylic resins,[20,24] so loss of stabilizer in these systems was not entirely unexpected. Most of the color seemed to be contained in the surface layer.

Comparison with Experiment. Determination of Wavelength Sensitivity Spectrum. The wavelength sensitivity spectrum for polystyrene was determined according to the method described above. The data were obtained by exposing unstabilized specimens of polystyrene protected by cutoff filters to radiation from a xenon arc lamp. The development of color was monitored by periodic color measurement on the specimens. The wavelength sensitivity spectra for polystyrene yellowing is shown in Figure 9.

Preparation of Samples. To assess the effectiveness of the model in predicting degradation rates, samples of polystyrene containing a variety of UV stabilizers were subjected to accelerated weathering. The stabilizers were chosen to represent a range of chemical structures. Samples were prepared at several stabilizer concentrations. The formulations used in this experiment are summarized in Table 2. Actual stabilizer loading levels were determined by gel permeation chromatography.

Two different sets of accelerated weathering conditions were employed. The conditions are summarized in Table 3. The principal difference between the conditions was the amount of ultraviolet light incident upon the samples: the xenon arc source with borosilicate inner and outer filters (condition A) has a short wavelength cutoff of approximately 295 nm, while the quartz/borosilicate filter combination (condition B) gives a cutoff of about 280 nm. The emission spectra of both sources were measured by Atlas Electric Devices for lamps similar to the ones used in this study. The samples exposed to the borosilicate/borosilicate filtered light were tested according to ASTM D2565, including an 18 min water spray every 2 h.

Color measurements were made on the samples after 0, 100, 300, 500, 750, and 1000 h of exposure using a Hunterlab Ultrascan color instrument in transmission mode, large area view, illuminant D_{65}, 10° observer, CIE L^*, a^*, b^* coordinates. The quantity of interest was the b-coordinate on the L, a, b color scale. Yellowing rates were determined by plotting Δb^* ($= b^*(t) - b^*(0)$) *vs* time. The slope of the best line through the points was taken as the yellowing rate. Results of linear regression on the yellowing *vs* time data are collected in Table 4.

Stabilizer Spectra. The spectra of the photostabilizers investigated in this study were recorded in acetonitrile solutions. A sample of TINUVIN 328 UV stabilizer was dissolved in acetonitrile and diluted with ethylbenzene to more closely approximate the nonpolar environment of the stabilizer in polystyrene. There were no striking differences in absorbance maxima or extinction coefficients between the acetonitrile and ethylbenzene solutions. The absorbance spectra were divided by the solution concentrations (in g/L) to obtain specific absorptivity as a function of wavelength.

Correlation of Predictions with Experiment. Yellowing rates were computed using eq 4 with the wavelength sensitivity spectrum in Figure 9 and the measured stabilizer concentrations. The correlation of experimental and predicted yellowing rates is presented in Figure 10. The plot includes all samples: varied stabilizer identity, concentration, and light source.

In the plot, points of the same shape (*e.g.*, squares) correspond to samples containing the same stabilizer. The solid circles represent unstabilized polystyrene, both virgin material and material that was double-passed through the compounding extruder.

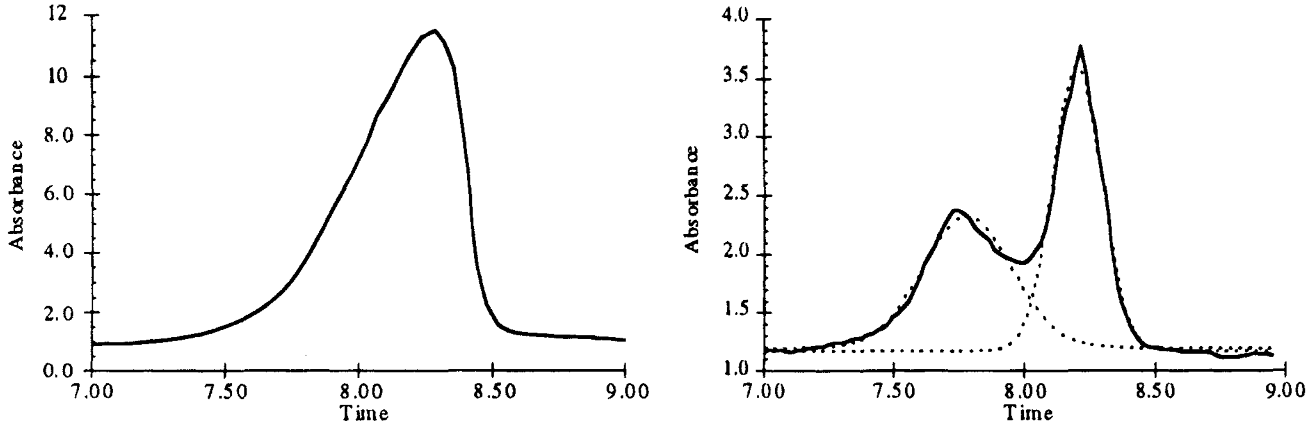


Figure 8. HPLC analysis of stabilizer permanence (a) concentration of TINUVIN 328 UV stabilizer in the bulk of an unweathered polystyrene sample and (b) concentration of TINUVIN 328 UV stabilizer in the top 30 μm of a sample weathered for 500 h in a quartz-borosilicate filtered xenon arc weathering device. The peak at 7.7 min is a color body that developed during the exposure.

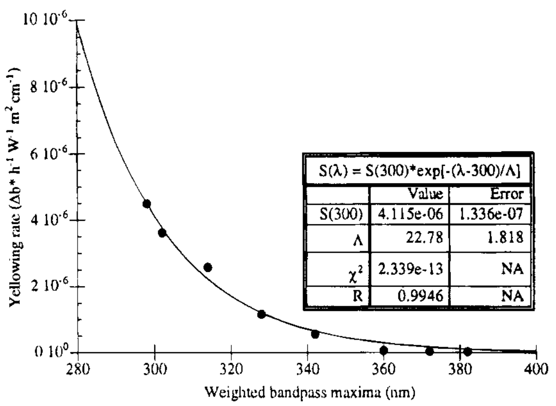


Figure 9. Wavelength sensitivity spectrum for polystyrene yellowing.

Figure 10 reveals a number of interesting points. The correlation between experimental and predicted rates—over different concentrations, chemical structures, and radiation sources—is quite good. However, the nonzero intercept and nonunity slope reveal a systematic underestimate by the model of the actual yellowing rate. Possible sources of the systematic error are discussed below. Within groups of samples containing the same stabilizer, the linear relationship between experimental and predicted yellowing rates appears to be better than the overall correlation. Thus, the model appears to predict well the dependence of yellowing rate on stabilizer concentration.

Figure 11 contains a plot of a subset of the data in Figure 10, representing different stabilizers at the same nominal concentration. Again, the correlation between experimental and predicted yellowing rates is good. The least-squares line through this subset of data nearly coincides with the line through all the data points in Figure 10. In this subset of data, the differences in predicted yellowing rates arise principally from differences in the absorbance spectra of the stabilizers. Thus, we conclude that the model represents fairly the important mechanism of stabilization in these additives, and we conclude that the screening approximation (approximation 3 above) is reasonably accurate.

Conclusions

(1) A general model for photodegradation of transparent polymers has been developed.

(2) The model predicts dependence of polystyrene yellowing on stabilizer identity, concentration, and light source spectrum reasonably well.

(3) New understanding of variables such as concentration, part thickness, and stabilizer absorption has been gained.

(4) The time-dependence of the stabilizer concentration cannot be ignored.

Experimental Section

Materials. The polystyrene used in these experiments was STYRON 685 polystyrene produced by the Dow Chemical Co. Stabilizers were commercial samples obtained from the respective manufacturers: TINUVIN P, TINUVIN 234, TINUVIN 328, Ciba Additives; CYASORB 531, CYASORB 1164, CYASORB 5411, Cytec.

Instrumentation. Schott glass cutoff filters were purchased from Melles Griot. The following Schott glass types were used: WG280, WG295, WG305, WG320, WG335, WG345, WG360, GG375, GG385, GG395, the number indicating the approximate wavelength (in nm) for 50% transmittance. Optical spectra for stabilizers and for Schott glass cutoff filters were determined on a Hewlett-Packard Model 8452A UV–vis spectrophotometer. Samples were subjected to accelerated weathering in Atlas Electric Devices Model Ci65 xenon arc Weather-Ometers under the conditions specified in the text. Gel permeation chromatography was run on a Hewlett-Packard Model 1090 chromatograph equipped with diode array UV–vis detection, and 10 μm crosslinked polystyrene columns from Polymer Laboratories. THF was used as the mobile phase at a flow rate of 1 mL/min. Determination of stabilizer concentrations was accomplished by running calibration standards of the absorbers and monitoring absorbance at 300 nm. Color measurements were made on a Hunterlab Ultrascan color instrument.

Stabilized Polystyrene Yellowing. Polystyrene samples were compounded with stabilizers to give nominal concentrations of 0.02, 0.06, and 0.2%. Actual stabilizer loading levels

Table 2. Formulations Used in Preparing Polystyrene Samples for Accelerated Photodegradation

sample	additive	chemical class	nominal loading (wt %)	measured loading (wt %)
1	none	virgin STYRON 685 polystyrene resin	0	
2	none	dbl. passed STYRON 685 polystyrene resin	0	
3	TINUVIN 328	benzotriazole	0.02	0.022
4	TINUVIN 328	benzotriazole	0.06	0.063
5	TINUVIN 328	benzotriazole	0.20	0.233
6	CYASORB 531	benzophenone	0.02	0.078
7	CYASORB 531	benzophenone	0.06	0.085
8	CYASORB 531	benzophenone	0.20	0.258
9	CYASORB 1164	triazine	0.02	0.024
10	CYASORB 1164	triazine	0.06	0.057
11	CYASORB 1164	triazine	0.20	0.18
12	TINUVIN P	benzotriazole	0.06	0.049
13	TINUVIN 234	benzotriazole	0.06	0.043
14	CYASORB 5411	benzotriazole	0.06	0.049

Table 3. Summary of Accelerated Weathering Conditions Used for Testing Stabilized Polystyrene Samples

condition	A	B
irradiance	0.35 W/m^2 at 340 nm	0.35 W/m^2 at 340 nm
filter combination	borosilicate inner filter borosilicate outer filter (P-type)	quartz inner filter borosilicate outer filter (S-type)
water spray	102 min light, 18 min light + water spray	light only, no water spray
black panel temp (°C)	63	63
wet bulb depression (°C)	10	10
conditioning water temp (°C)	40	40

Table 4. Yellowing Rates of Stabilized Polystyrene Samples

sample	stabilizer	concn^a (wt. %)*	yellowing rate (Δb^*/h)	intercept ($\Delta b^*_{t=0}$)	*R*
1A	none		0.016 949	−0.1286	0.986 88
2A	none		0.0176	0.584 76	0.988 47
3A	TINUVIN 328	0.022	0.014 496	0.556 41	0.984 88
4A	TINUVIN 328	0.063	0.012 621	0.215 78	0.957 35
5A	TINUVIN 328	0.233	0.008 908 6	0.780 15	0.916 94
6A	CYASORB 531	0.078	0.013 384	0.691 03	0.977 52
7A	CYASORB 531	0.085	0.014 922	0.138	0.962 36
8A	CYASORB 531	0.258	0.011 28	0.661 37	0.930 98
10A	CYASORB 1164	0.057	0.011 625	0.463 57	0.964 12
11A	CYASORB 1164	0.18	0.008 9027	1.0044	0.9251
12A	TINUVIN P	0.049	0.011 409	0.002 697 9	0.953 75
13A	TINUVIN 234	0.043	0.013 346	0.171 25	0.977 08
14A	CYASORB 5411	0.049	0.012 967	−0.032 881	0.968 44
1B	none		0.020 031	1.1001	0.990 94
2B	none		0.018 929	1.9238	0.982 57
3B	TINUVIN 328	0.022	0.017 331	1.3303	0.988 53
4B	TINUVIN 328	0.063	0.015 552	0.938 89	0.986 47
5B	TINUVIN 328	0.233	0.011 929	1.2743	0.976 65
6B	CYASORB 531	0.078	0.016 065	1.4512	0.984 67
7B	CYASORB 531	0.085	0.016 27	1.322	0.985 56
8B	CYASORB 531	0.258	0.013 238	1.4777	0.974 77
9B	CYASORB 1164	0.024	0.018 465	1.1409	0.991 26
10B	CYASORB 1164	0.057	0.015 319	1.192	0.984 83
11B	CYASORB 1164	0.18	0.012 516	1.4679	0.975 46
12B	TINUVIN P	0.049	0.014 265	0.7757	0.983 73
13B	TINUVIN 234	0.043	0.015 908	1.0076	0.987 86
14B	CYASORB 5411	0.049	0.015 861	0.713 36	0.986 71

^{a} As determined by gel permeation chromatography measurements on molded samples at $t = 0$.

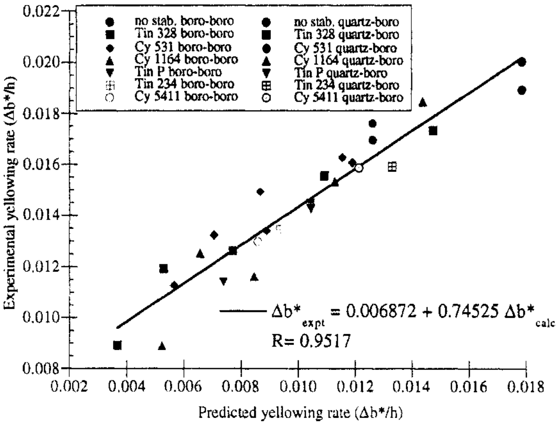


Figure 10. Correlation of experimental and predicted yellowing rates for stabilized polystyrene samples.

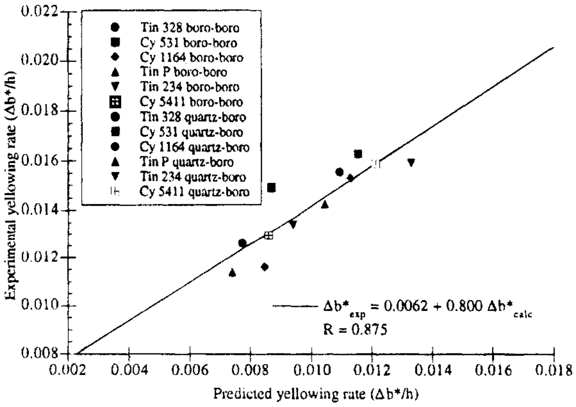


Figure 11. Correlation of experimental with predicted yellowing rate for stabilized polystyrene: effect of stabilizer structure.

were determined by gel permeation chromatography. The quantities used are listed in Table 5. The samples were compounded in a Welding Engineers twin-screw compounding extruder, pelletized, and passed again through the extruder to improve the distribution of the stabilizer in the polymer.

Table 5. Quantities Used in Preparing Stabilized Polystyrene Specimens

sample	additive	chemical class	g of additive in 1 kg of PS
1	none		0
2	none		0
3	TINUVIN 328	benzotriazole	0.200
4	TINUVIN 328	benzotriazole	0.600
5	TINUVIN 328	benzotriazole	2.004
6	CYASORB 531	benzophenone	0.200
7	CYASORB 531	benzophenone	0.600
8	CYASORB 531	benzophenone	2.004
9	CYASORB 1164	triazine	0.200
10	CYASORB 1164	triazine	0.600
11	CYASORB 1164	triazine	2.004
12	TINUVIN P	benzotriazole	0.600
13	TINUVIN 234	benzotriazole	0.600
14	CYASORB 5411	benzotriazole	0.600

The samples were injection-molded to make 2 × 3 in rectangles of 100-mil thickness. The specimens were cut and mounted in Atlas Electric Devices Ci65 xenon arc Weather-Ometers under the conditions described in the text. Initial yellowness values were taken at 0 h, and individual specimens were withdrawn for yellowness measurement after 100, 200, 300, 500, 750, and 1000 h.

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