

Calculation of the Efficiency of Ultraviolet Screeners in Plastics

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Synopsis

Calculation of the effect of light absorbers (UV screeners) on the photochemistry of polymers shows that a critical factor in reducing the rate of photodegradation is the thickness of the actual degraded layer. When the degradation is confined to a zone within a few microns of the exposed surface, the efficiency of light absorption as a stabilization mechanism is greatly reduced. The relative absorptivity of the base resin and pigment loadings are calculated to have a minor effect on stabilization efficiency for polymers having thin layers of degradation.

INTRODUCTION

Light-absorbing compounds often are added to plastics to screen out damaging ultraviolet (UV) light and thereby to extend the useful lifetime of articles made of the resin. It seems reasonable that the addition of a compound that absorbs much more of the harmful light than the base polymer should greatly reduce the rate of photodegradation. However, one often finds that even large loadings of UV screeners do not significantly increase the photostability of a sample. There are several reasons why this may be so: the screener may not in fact absorb the harmful wavelengths of light; the screener may not efficiently and harmlessly dissipate the energy it absorbs, and this could lead to destruction of the screener or cause other photochemistry to occur; the screener may be incompatible with the resin, migrate to the surface, and be lost. These are all problems that can, in principle, be solved by the use of a cleverly designed UV screener. However, a more serious problem can be that the degradation can be confined to a zone so thin that no UV screener, no matter how cleverly designed, can significantly reduce the rate of photodegradation. This inherent limitation on the performance of UV screeners has been largely ignored.

Although methods for calculating the efficiency of UV screeners in films have been described,¹⁻⁴ the usefulness and significance of these calculations seem to have been generally unappreciated. This paper is a reanalysis of the effect of a UV screener on the penetration of light into a plastic part and an examination of the importance of polymer absorption, pigment loading, and depth of degradation on the efficiency of UV screeners.

DISCUSSION

For the purposes of this analysis, it will be useful to consider the hypothetical case of a polymer film 50 μm thick in which the absorption due to the polymer or reactive impurities is 0.1 (79.5% transmission) at some actinic

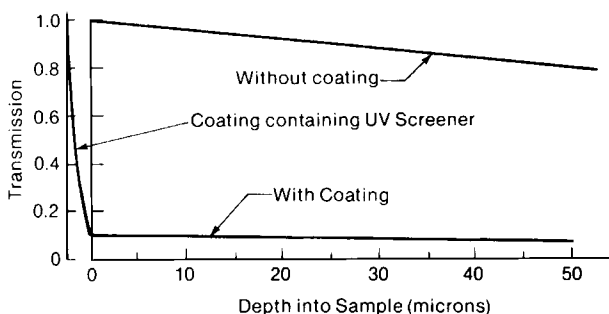


Fig. 1. Calculated transmission of light through a hypothetical polymer in the absence and presence of a coating that absorbs 90% of the incident light.

wavelength, say 330 nm. The UV screener will be assumed to have a molecular extinction coefficient (ϵ) of 10,000 at 330 nm and a molecular weight of 300, typical of 2-hydroxy-4-alkoxybenzophenones.

Coating

In the first case, it will be assumed that the degradation is uniform throughout the thickness of the sample and that the UV screener has been applied as a coating on the surface such that the absorbance at 330 nm is 1.0 (10% transmission) as shown in Figure 1. The effect of the UV screener in this case is to reduce the light intensity by 90% uniformly across the thickness of the sample. If the rate of photodegradation is linearly dependent on the incident light intensity, one would expect that the degradation processes would be slowed by a factor of 10 throughout the sample. The total amount of degradation at very long exposure times and the mode of failure would not be expected to have changed, but the time to failure should be 10 times longer than without the screener.

Bulk Additive

A quite different profile results from the same amount of screener used as a bulk additive as shown in Figure 2. In this case, the loading would be about 0.6 weight% in order to achieve a screener absorbance of 1.0 through a 50- μm sample. When the screener is used in the bulk, the light intensity is substan-

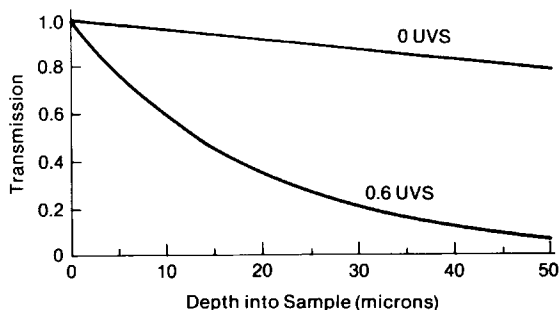


Fig. 2. Calculated transmission of light through a relatively nonabsorbing polymer in the absence and presence of 0.6 part by weight of UV screener.

tially reduced deep in the sample but is little changed near the exposed surface, and calculating the expected effect on the rate is more difficult.

For systems in which the rate of degradation is linearly dependent on the light intensity, the rate at any depth, k_ℓ , is proportional to the light intensity at that depth, I_ℓ .

$$k_\ell \propto I_\ell \quad (1)$$

If the Beer-Lambert law is obeyed then the light intensity at any depth is given by Eq. (2) in which the extinction coefficient, ϵ , multiplied by the concentration of all the absorbing species, C , must be considered.

$$I_\ell = I_0 10^{-\Sigma \epsilon C \ell} \quad (2)$$

Since $k_\ell \propto I_\ell$, then

$$k_\ell \propto 10^{-\Sigma \epsilon C \ell} \quad (3)$$

The total rate for the system will be the integral of all the rates given by Eq. (3) from $\ell = 0$ (the surface) to the total thickness of the film, L .

$$k \propto \int_0^L k_\ell d\ell \quad (4)$$

$$k \propto \int_0^L 10^{-\ell \Sigma \epsilon C} d\ell \quad (5)$$

Integration gives

$$k \propto \int_0^L \frac{10^{-\ell \Sigma \epsilon C}}{-\Sigma \epsilon C} \quad (6)$$

Evaluation of the integral gives

$$k \propto \frac{1}{\Sigma \epsilon C} - \frac{10^{-L \Sigma \epsilon C}}{\Sigma \epsilon C} \quad (7)$$

Substituting $10^{-L \Sigma \epsilon C} = T_L$ and $A_L = L \Sigma \epsilon C$ gives

$$k \propto \frac{L}{A_L} - \frac{L T_L}{A_L}$$

$$k \propto \frac{L}{A_L} (1 - T_L) \quad (8)$$

where A_L is the absorbance and T_L is the transmission of the film. The ratio of the stabilized to the unstabilized rates is given by Eq. (9) where the subscript "s" corresponds to the stabilized values and "o" corresponds to the unstabilized values of the transmission and absorbance.

$$\frac{k_s}{k_o} = \frac{(1 - T_s) A_o}{(1 - T_o) A_s} \quad (9)$$

A and T are not independent variables since $A = -\log T$, and since both are functions of the thickness of the film, L , the thickness remains an important

variable. Equation (9) is mathematically equivalent to the "protective effectiveness"^{2,3} and ratios of "light absorbed by the polymer"⁴ previously described.¹

In applying Eq. (9) to the problem in Figure 2, $A_o = 0.1$, $A_s = 1.1$, $T_o = 0.795$, and $T_s = 0.0795$. This gives $k_s/k_o = 0.41$ compared to $k_s/k_o = 0.1$ for the case in Figure 1. In other words, while the screener applied as a coating may be expected to extend the lifetime by a factor of 10, the bulk-added screener could extend it by a factor of only 2.5.

Surface Degradation

A key assumption in this analysis is that the degradation was uniform throughout the 50- μm thickness of the sample. This is rarely, if ever, the case in real-world polymers. In polypropylene, for example, the degradation extends only 3–5 μm from each surface.⁵ The depth of degradation may be limited by the presence of sensitizing impurities, rates of oxygen diffusion, or light absorption by the degradation products. If an estimate of the depth of degradation at the failure time can be made, that value should be used for L . If one assumes that the degradation occurs uniformly over 5 μm in the case of Figure 2 ($A_o = 0.02$ and $A_s = 0.22$), then application of Eq. (9) gives $k_s/k_o = 0.89$. If the degradation were confined to the top 1 μm , then $k_s/k_o = 0.98$. That is, the thinner the degradation layer, the less effective a light screener can be in stabilizing the polymer. For the system described, k_s/k_o for various UV screener loadings as a function of thickness of the degradation layer is shown in Figure 3. One sees that even massive amounts of UV screener cannot slow the degradation rate very much when the degradation layer is less than 5 μm thick if the additive works by light absorption alone.

The example described above is for a relatively nonabsorbing polymer—one with an absorbance of only 0.1 at 330 nm for a 50- μm section. The light penetration curves for a more highly absorbing system with $A_o = 1.0$ at 50 μm are shown in Figure 4. As before, the curve with the screener is for a loading of 0.6 parts by weight so that the additional absorption at 50 μm due to the screener is 1.0. In this case, the degradation will inevitably be nearer to the surface because not much light penetrates deeply into the sample. Although it appears that the added screener does not contribute much to diminishing the light penetration, one finds that the rate reductions as a function of the thickness of the degradation layer (Fig. 5) are not much

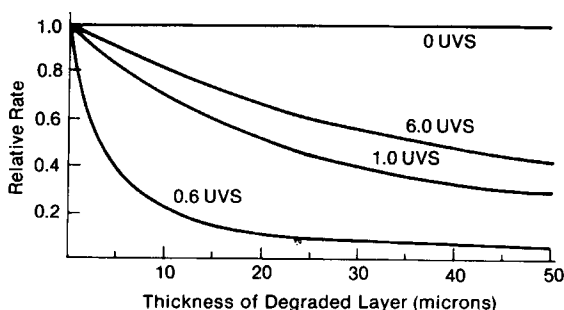


Fig. 3. Calculated rate reductions due to various loadings of UV screener as a function of thickness of the degraded layer in a relatively nonabsorbing polymer.

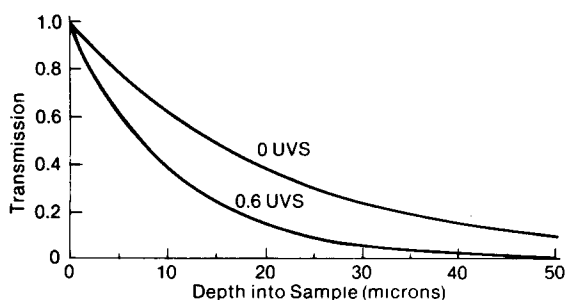


Fig. 4. Calculated light transmission through a highly absorbing polymer in the absence and presence of 0.6 parts by weight of UV screener.

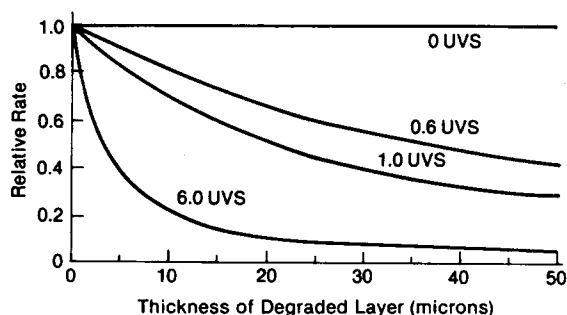


Fig. 5. Calculated rate reductions due to several loadings of UV screener in a highly absorbing polymer as a function of thickness of the degraded layer.

different from those in Figure 3 at depths of 20 μm or less. That is, a highly absorbing polymer and a slightly absorbing polymer are nearly equally difficult to stabilize if the depths of degradation are the same. Of course, highly absorbing systems are likely to have thin layers of degradation, but as in the case of polypropylene, essentially nonabsorbing polymers can have very thin degradation layers as well. Contrary to what one might intuitively expect, the relative extinction coefficients of the polymer and the screener are largely irrelevant. The key variable is the experimentally determined depth of degradation.

Filler Effects

Many applications of polymers require that pigments be added to the resin. The result is diminished light penetration since pigment particles can scatter, reflect, and absorb light. If one assumes that the particles are totally absorbing spheres and neglects scattering, then the fraction of light transmitted to any depth ℓ is given by Eq. (10) where V is the volume fraction of the pigment and d is the particle size. The $3/2$ factor arises from the assumption of a spherical rather than cubic particle shape, and the $(1 - 3/2V)$ term represents the probability of a photon not encountering a particle in a slice of thickness d . This value must be multiplied ℓ/d times to arrive at the probability of a photon not encountering a particle up to depth ℓ .⁷

$$I_{\ell}/I_0 = (1 - 3/2V)^{\ell/d} \quad (10)$$

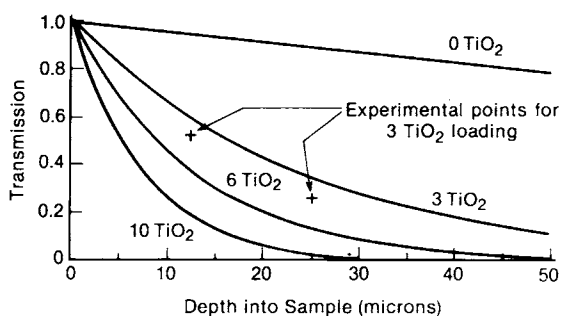


Fig. 6. Calculated effect of TiO_2 loading on the transmission of light into a relatively nonabsorbing polymer. The crosses are experimentally determined from diffuse transmission spectra of polystyrene/polyphenylene oxide films containing 3 parts by weight of TiO_2 .

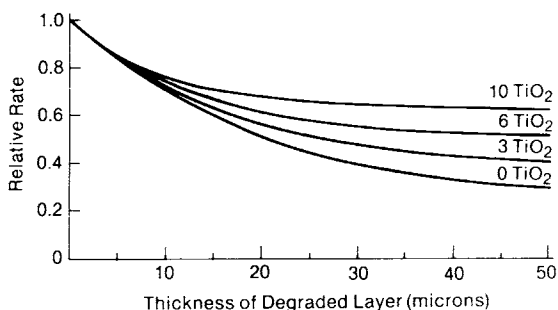


Fig. 7. Calculated rate reductions due to one part of UV screener as a function of degraded layer thickness for several loadings of TiO_2 pigment. The effectiveness is not affected significantly for thicknesses less than $10 \mu\text{m}$.

Considered in this way, the pigment itself is a screener and will tend to decrease the rate of degradation and localize it toward the surface. Figure 6 shows the light penetration into a relatively nonabsorbing polymer containing various levels of TiO_2 . For rutile TiO_2 , the particle size is about $0.2 \mu\text{m}$ and the density is about 4. It is essentially totally absorbing at wavelengths less than 360 nm . Also on Figure 6 are two points from diffuse transmission spectra of polystyrene/polyphenylene oxide films containing 3 pbw of TiO_2 . The agreement with the calculated transmission is good. Figure 7 shows how the effectiveness of 1 weight% of UV screener is diminished as the pigment loading is increased. Significant differences occur only at depths greater than $10 \mu\text{m}$. For thin layers of degradation, little difference in rate reduction is expected as the pigment loading is increased. Again, the thickness of the degraded layer remains as the key variable for the effectiveness of a UV screener.

CONCLUSIONS

This analysis has two important implications for experiments involving UV screens. The first is that the commonly used practice of irradiating an unstabilized film through one containing a UV screener in an effort to separate screening effects from other possible effects (using the situation in Fig. 1 to simulate Fig. 2) cannot give quantitative results. Even if one adjusts

the concentration of screener in the filtering film so that the proper amount of light passes through the sample film,⁴ one cannot reproduce the light intensity gradient through the cross section of the film that will cause a change in the distribution of the degradation. Reasonable results will be obtained only in cases in which the additive is ineffective as a light absorber, as in polypropylene where essentially no stabilization of the sample film is seen.^{4,6} In cases in which light absorption by the UV screener is important, one will tend to overestimate the importance of the screener because degradation near the surface of the test film will be disproportionately decreased. This can be especially significant when surface-sensitive properties such as embrittlement times or impact strength are being measured. When the screener is applied over the surface, the surface can be effectively screened and stabilized while a bulk-added screener leaves the surface relatively unprotected. The way a screener changes the photochemistry as a bulk additive cannot be simulated by using it as a coating or filter.

The second implication is that UV screeners will always be relatively ineffective in a large number of cases. When pigment loadings or the inherent absorptivity of the polymer restricts the degradation to within a few microns of the surface, stabilization by light absorption cannot be very effective. One must count on energy quenching or radical scavenging by the additive if it is to show significant effect. This evidently is what happens in polypropylene.⁶ However, many polymers degrade through mechanisms that do not lend themselves to such effects. In situations such as these, only modest improvements may result even at large screener loadings.

In summary, the effectiveness of bulk-added UV screeners is sharply limited by the thickness of the degradation layer if they can act by light absorption alone. Although in some cases these additives can exhibit great effectiveness by acting through other mechanisms, there is no reason to expect similar results for all polymers. If UV screeners show little effectiveness in a polymer system, and it has been determined that the screener is in fact absorbing the actinic light, then the reason could very well be that the depth to which degradation must occur to cause failure is so small that no screener can be effective in reasonable amounts as a bulk additive.

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