

# Light Stabilization of Polymers Using Opaque Pigments

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## Synopsis

The ultraviolet light screening characteristics of monodisperse and polydisperse opaque spherical pigment particles are examined in the nonreflection limit. The screening capability for polydisperse particle size distributions is most uniquely described in terms of the area-average radius. The light screening is related to the pigment's area-average radius and volume fraction loading. Light intensity as a function of depth is stated for systems containing an opaque pigment and a soluble UV light absorber.

## INTRODUCTION

Premature failure of polymers used in outdoor applications is prevented usually by the use of light stabilizers which act either by (a) controlling the amount of light which reaches the bulk of the polymer, or (b) interaction/reaction with various products of initial polymer photoreaction (such as excited molecular species, radicals, and hydroperoxides) which lead to autocatalytic degradation.<sup>1</sup> The former class of stabilizers consists of light absorbers and light screeners selected on the basis of their extinction coefficients (or the degree of opacity in the case of particulate screeners) in the near ultraviolet region of the spectrum, the spectral region responsible for the light-induced deterioration of the polymers.

Light absorbers such as the benzotriazoles compete with the polymer for absorption of the ultraviolet radiation and are able to harmlessly dissipate the light energy. Such systems are easily modeled by the use of the well known Beer-Lambert law. The relative effectiveness of light absorbers when incorporated in a top-coat or distributed uniformly throughout the bulk of the polymer has been examined.<sup>2,3</sup> An attempt to quantify the effect of progressive development of light-absorbing reaction products on light-initiated reactions has been made.<sup>4</sup>

However, the case of polymer systems stabilized by particulate light screeners (usually inorganic pigments or carbon black) has been studied comparatively little. Yet a wide variety of polymer products used in outdoor applications are included in this category. Examples include poly(vinyl chloride) compounds used in siding, window frame, and exposed pipe applications, flexible roofing membranes of both plasticized PVC and

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ethylene-propylene-diene monomer (EPDM) rubber, and glass/silica filled unsaturated polyester compositions.<sup>5,6</sup>

The aim of the present work is to derive a simple relevant expression for the attenuation of light passing through a polymer stabilized by opaque, spherical pigment particles. The effect of light attenuation by such particles, by added molecular UV absorbers, and by the polymer on light intensity within a polymer composite is briefly examined.

### THEORETICAL

The initial model considers a polymer matrix which is essentially transparent in the ultraviolet region of the solar spectrum and which is stabilized using a volume fraction  $V$  of a polymer-insoluble pigment composed of monodisperse spheres of radii  $r$ . To be effective in stabilizing the polymer matrix, the pigment particles must have a very large absorption coefficient (at the relevant wavelengths of light) compared to that of the polymer. As a first approximation, the particles are assumed to be infinitely absorbing (opaque). To facilitate the approximate calculation of the light intensity/depth relation, we arbitrarily replace the actual random distribution of the pigment particles in three dimensions by a random distribution of the particles in two dimensions within lamina of thickness  $2r$ . Thus, although the volume fraction of the pigment within a lamina is equal to the average volume fraction throughout the system, there is a periodicity of concentration in the direction of light transmission normal to the surface.

If the pigment volume fraction is  $V$ , the number of pigment spheres in a lamina volume  $y \times y \times 2r$  cm<sup>3</sup> is  $N = 2ry^2V/[(4/3)\pi r^3]$ . The total cross-sectional areas of these  $N$  spheres divided by  $y^2$  equals the fraction of light removed in passing through the lamina:  $A = N\pi r^2/y^2$ , or  $A = 3V/2$ . In passage from the incident surface to depth  $L$  the light traverses  $n = L/2r$  laminae. The light intensity at depth  $L$  is, therefore,

$$I_L = I_0(1 - 3V/2)^{L/2r} \quad (1)$$

This expression has been independently obtained by Pickett.<sup>7</sup>

The foregoing assumes complete opacity of the pigment to all incident light wavelengths of interest, as well as a uniform geometry (spherical) and particle size for the pigment fraction. Most common pigments are in fact nearly opaque in the ultraviolet region of the spectrum. Approximating such materials by totally opaque spheres is therefore not unreasonable. Also implicit in the treatment is the lack of significant reflection of the light at the pigment/matrix interface. The reflectivities of common pigments (such as titanium dioxide) are high in the visible region of the spectrum, but become low in the near ultraviolet region of concern with respect to polymer degradation. Any reflections by the particles will increase the total light flux in the polymer near the surface and cause the light intensity to decrease less rapidly than predicted by eq. (1).

The model just used to obtain eq. (1) assumed monodisperse spherical pigment particles. We wish now, using the same formalism, to investigate the light attenuation due to pigment consisting of opaque spherical particles

having a number fraction distribution of radii lengths expressed by  $N(r)$ . We resort to defining the lamina thickness as  $2r_x$ , where  $r_x$  is an average radius defined by

$$r_x = \int_0^\infty r^x N(r) dr / \int_0^\infty r^{x-1} N(r) dr, x \geq 1 \tag{2}$$

For  $x = 1, 2, 3,$  and  $4,$  respectively,  $r_x$  is the number-average, length-average, area-average, and volume-average radius.

Requiring the centers of the spherical particles to lie in the midplane of the lamina (to preclude intralaminar eclipsing of particles), the number of particles lying "within" a volume  $y \times y \times 2r_x$  cm<sup>3</sup> in a polymer containing volume fraction  $V$  of pigment is

$$N = 2r_x y^2 V / \int_0^\infty (4/3) \pi r^3 N(r) dr \tag{3}$$

The fractional area obscured by these  $N$  particles in the  $y^2$  cm<sup>2</sup> area is

$$A = N \int_0^\infty \pi r^2 N(r) dr / y^2 = (3/2) V r_x / r_3 \tag{4}$$

Therefore, the light intensity at depth  $L$  (cm) in such a pigmented polymer is

$$I_L = I_0 [1 - (3/2) V r_x / r_3]^{L/2r_x} \tag{5}$$

Inspection of eq. (5) indicates that calculated  $I_L$  will differ slightly depending on what  $r_x$  is chosen to define the lamina thickness. Defining the lamina thickness as  $2r_3$ , i.e., twice the area-average radius, one obtains a unique expression, formally identical to eq. (1), and dependent on the sphere size distribution form and breadth only insofar as the area-average radius is not normally directly measured:

$$I_L = I_0 (1 - 3V/2)^{L/2r_3} \tag{6}$$

If  $N(r)$  is satisfactorily approximated by a gamma distribution function

$$N(r) = r^\alpha \exp(-r/\beta) / [\beta^{\alpha+1} \Gamma(\alpha + 1)] \tag{7}$$

$\alpha > -1,$   $\beta = r_1 / (\alpha + 1),$  and the various average radii are related by

$$r_1 : r_2 : r_3 : r_4 : : \alpha + 1 : \alpha + 2 : \alpha + 3 : \alpha + 4 \tag{8}$$

with

$$\alpha = (r_1/\sigma)^2 - 1 \tag{9}$$

Measurement of  $r_1$  and  $\sigma$  for a given polydisperse pigment then permits calculation of the area-average radius  $r_3$ , needed for eq. (6).

$$r_3 = r_1 + 2\sigma^2/r_1 \tag{10}$$

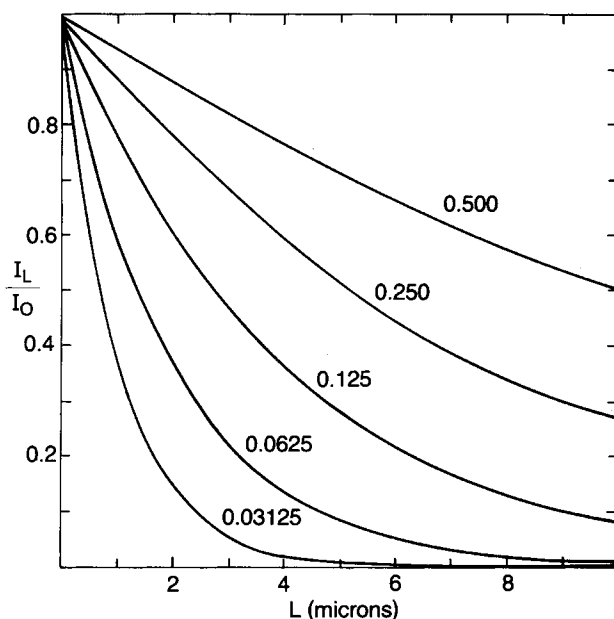


Fig. 1. The dependence of light intensity at a depth  $L$  ( $\mu\text{m}$ ) from the polymer surface upon the particle radii ( $\mu\text{m}$ ) indicated for each curve.  $V = 0.04$ ,  $k_p = 0.008 \mu\text{m}^{-1}$ , and  $c_a = 0$ .

Introducing into eq. (6) the attenuation of light in the polymer matrix due to its absorption by the polymer and by any added soluble UV absorber, one arrives at the expression

$$I_L = I_0(1 - 3V/2)^{L/2r_3} \exp[-(k_p + k_a)L] \quad (11)$$

With  $L$  and  $r_3$  expressed in cm,  $k_p$  ( $\text{cm}^{-1}$ ) is the linear absorption decrement of the polymer and  $k_a$  ( $\text{cm}^{-1}$ ) =  $2.303\epsilon_a c_a$  ( $\text{cm}^{-1}$ ) is the linear absorption decrement of the UV-absorbing additive with  $c_a$  ( $\text{mol}^{-1}$ ) the additive concentration and  $\epsilon_a$  ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ ) the additive's extinction coefficient.

The light attenuation due to an opaque, nonreflecting pigment is equal to the attenuation due to light absorption due to a soluble UV light absorber when

$$-\ln(1 - 3V/2)/2r_3 = 2.303\epsilon_a c_a \quad (12)$$

The light screening ability of a pigment is strongly dependent on the size of the pigment particles. This is obvious in eq. (11) where the reciprocal of  $r_3$  appears in the exponent. Figure 1 illustrates the particle size dependence of  $I_L/I_0$  vs.  $L$  at a pigment volume fraction of 0.04 in a polymer having  $k_p = 0.008 \mu\text{m}^{-1}$  in the absence of a soluble UV absorber. The dependence of screening effectiveness on the loading (volume fraction) of pigment is less dramatic within the normally practical loading range. Figure 2 presents  $I_L/I_0$  vs.  $L$  in the system just described at a constant area-average particle radius,  $r_3 = 0.125 \mu\text{m}$ , at pigment volume fractions in the 0.00–0.05 range. A final

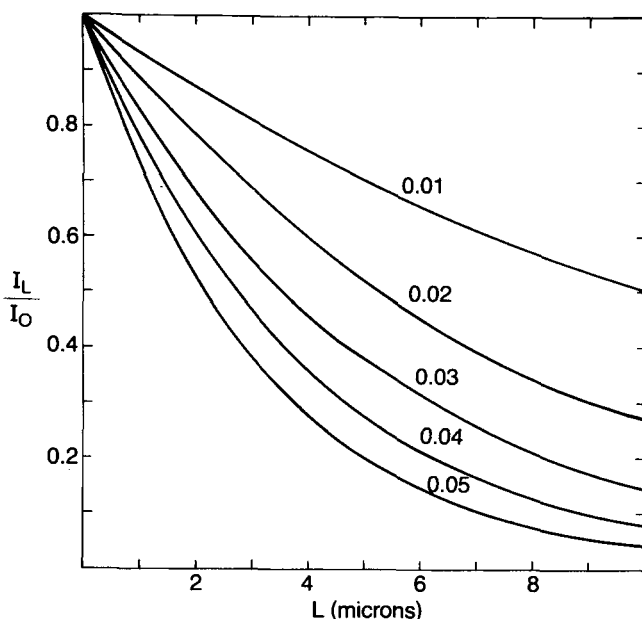


Fig. 2. Variation of the light shielding effect of a pigment with the volume fraction of incorporated pigment (indicated for each curve). The area-average radius of the spherical pigment particles is  $r_3 = 0.125 \mu\text{m}$ .  $k_p = 0.008 \mu\text{m}^{-1}$  and  $c_a = 0$ .

illustration of the screening by pigment and soluble UV absorber individually and in combination is shown in Figure 3, where practical levels of the additives are introduced into a rather transparent polymer.

## DISCUSSION

The model developed in the above section is best tested using optical transmittance data for polydisperse particles in a transparent matrix. Such data is not presently available. However, the photodegradation of polymers is determined by the light screening effectiveness of pigments in the polymer. Therefore, the experimental data in the literature on light-induced deterioration of polymers must show qualitative agreement with the predictions based on the model. The complexity of the weathering phenomenon and the lack of information regarding the intensity dependence of the deterioration process precludes a quantitative analysis of such data.

Both eq. (6) and Figure 1 indicate the light attenuation to be relatively rapid, implying that the degradation of filled polymers will occur mostly in the surface layers. (This is also true in the case of polymers containing UV absorbers.) In the case of polyethylene/2% carbon black system the oxidation was found to be localized mostly in a "skin" layer 10–15 mils thick.<sup>8</sup>

In general, pigments of smaller average particle size impart superior stability against photodegradation of polymer. Wallder et al.<sup>9</sup> found the efficiency of protection of polyethylene (against photoinduced loss of flexibility) by carbon black increased markedly with decreasing particle size of the black used. This observation is consistent with the equations derived in the theoretical section. Similar observations have been made by others.<sup>10,11</sup>

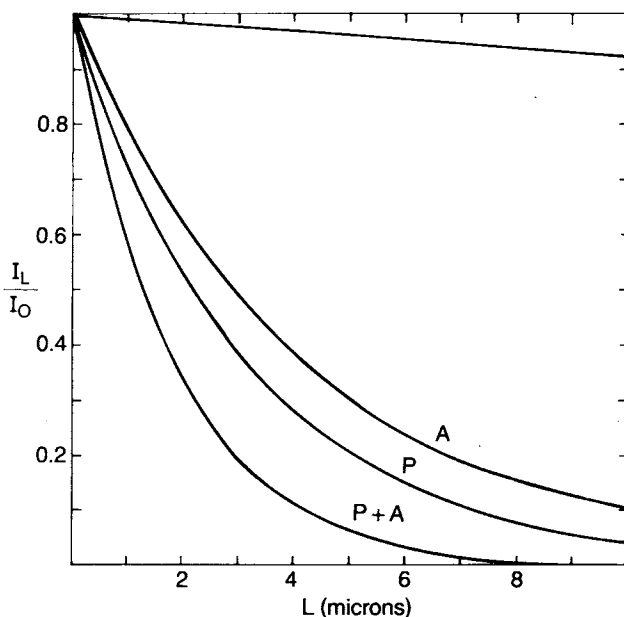


Fig. 3. The dependence of light intensity at a depth  $L$  ( $\mu\text{m}$ ) from the polymer surface upon UV absorber and pigment loading. Upper curve: no additives,  $k_p = 0.008 \mu\text{m}^{-1}$ . A curve: 0.05 mol/L of UV absorber having  $MW = 200$  and absorption coefficient,  $\epsilon_a = 2 \text{ L/mol } \mu\text{m}$ .  $k_p = 0.008 \mu\text{m}^{-1}$ . P curve: opaque, spherical pigment particles ( $r_3 = 0.1 \mu\text{m}$ ) incorporated at volume fraction,  $V = 0.04$ .  $k_p = 0.008 \mu\text{m}^{-1}$ . A + P curve: the same polymer containing both UV absorber and pigment at levels just described.

The light available to surface layers of polymer in the presence of a given volume fraction of pigment is given by eq. (6). The residual light at a given depth is a decreasing nonlinear function of the volume fraction of pigment in the matrix. Thus, a similar nonlinearity might be expected in the case of light-induced deterioration in polymers containing different extents of pigments. The data reported by Summers<sup>12</sup> on the yellowing of PVC [poly(vinyl chloride)] compositions containing 0–20 parts per hundred of titanium dioxide pigment illustrates the dependence of degradation on volume fraction of filler. The extent of yellowing decreased exponentially with the volume fraction of pigment.

We have been considering the protection of a polymer by soluble UV stabilizers and by opaque pigments to arise simply from the light screening effect. UV absorbing stabilizers may afford protection against photodegradation greater than that expected solely on the basis of light attenuation.<sup>13,14</sup> It should also be recognized that the protective effect provided by the spherical pigment particles as calculated above is a maximum possible effect. Both a lack of complete opacity and the presence of light reflection at the matrix/pigment interface will cause higher light intensities in the polymer than calculated in the simple limiting case treated. In particular, the light intensity very near the surface can be higher in the presence of reflective pigments than in their absence. Pigments and other fillers contribute to the mechanical properties of a polymer in addition to contributing to light

attenuation.<sup>15</sup> The choice of soluble UV stabilizers and/or light-obscuring particulate fillers for a given polymer application requires consideration of several attributes besides the primary one of light screening.

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