Protection of Polymers from Degradation by Ultraviolet Light: Compensation for Increased UV Light Intensity by Increased UV Absorber Concentration

In 1975 an attempt was made to estimate the costs associated with increased weathering of plastics due to specified increases in ultraviolet light intensities.[1] Gordon stated "a rule of thumb" existing in plastics technology that a doubling of a UV-absorbing protectant additive concentration is necessary to achieve the same useful lifetime of a plastic if a 50% increase in UV light intensity occurs. To generalize this rule for other intensities, it was postulated that a "characteristic depth" exists in polymer films stabilized for equal useful lifetimes by UV-absorbing protectants. At this depth the light intensity is kept the same when the incident light intensity increases by increasing the UV-absorbing protectant concentration. We wish here to examine the implications of the above rule of thumb and the generalizing postulate. In particular, we wish to see if there are any discernable reasons for the validities of the rule and its generalization.

Consider a polymer film which contains a UV absorber uniformly distributed throughout its volume. If the polymer absorption of monochromatic light incident normal to the film surface is characterized by an absorption decrement $k_p = 2.303\epsilon_p c_p$ and the UV-absorber absorption by an absorption decrement $k_a = 2.303\epsilon_a c_a$, the light intensity at depth L is given by

$$I_L = I_0 \exp\left[-\left(k_p + k_a\right)L\right] \tag{1}$$

where I_0 (photons cm^{-2} s^{-1}) is the intensity of the light entering the film surface.

Consider the incident light intensity increased by a factor x and the UV-absorber protectant concentration increased by a factor y. Then,

$$I_L = x I_0 \exp\left[-\left(k_p + y k_a\right)L\right] \tag{2}$$

The generalizing postulate says that there is a characteristic depth L_c, at which the light intensity expressed in eq. (1) ($x = 1$, $y = 1$) and in eq. (2) are equal when y has been correctly chosen to compensate for x. Combining the two expressions yields

$$L_c = (\ln x)/\left[k_a(y-1)\right] \tag{3}$$

Substituting this expression for the characteristic depth into eq. (2) yields for the light intensity at the characteristic depth

$$I_{L_c} = I_0 x^{-(1+k_p/k_a)/(y-1)} \tag{4}$$

The rule of thumb states that $y = 2.00$ when $x = 1.50$. Then according to eq. (3) the values of y needed to compensate for other values of x are

$$y = 1 + (\ln x)/(\ln 1.5) \tag{5}$$

The number of photons, E_p, absorbed by the polymer per cm^2 of surface to depth L after t (s) of irradiation is

$$E_p = I_0 t\left[x k_p/(k_p + y k_a)\right] \cdot \left\{1 - \exp\left[-\left(k_p + y k_a\right)L\right]\right\} \tag{6}$$
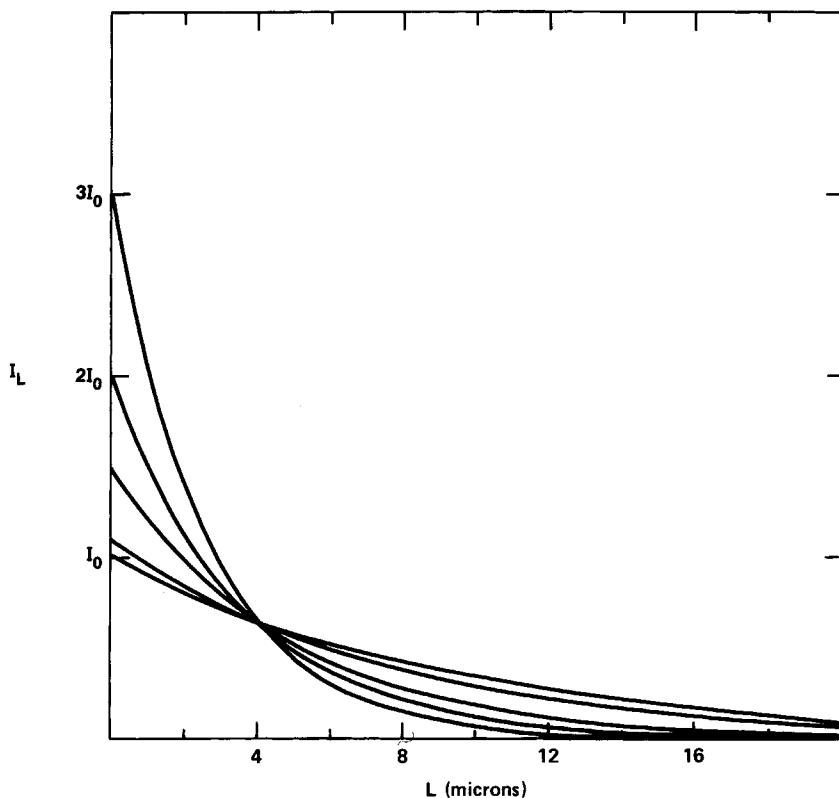
Fig. 1.   Light intensity as a function of depth for chosen x and the compensating y [eq. (5)] pairs. Polymer and absorber attenuation decrements are $k_p = 100$ cm^{-1} and $k_a = 1000$ cm^{-1}, respectively. x, y pairs are: 3.0, 3.710; 2.0, 2.710; 1.5, 2.000; 1.1, 1.235; 1.0, 1.000.

We assume that the degradation of the polymer is proportional to the number of photons absorbed by the polymer.

To exemplify the above relations, we display in Figure 1 light intensity as a function of depth [eq. (2)] for a system having $k_p = 100$ cm^{-1}, $k_a = 1000$ cm^{-1} and indicated x, y pairs [y is computed by eq. (5)]. The characteristic depth is $L_c = (\ln 1.5)/k_a$, or approximately 4 μm, at which the light intensity is $0.64 I_0$. At all depths less than 4 μm, the degradation of the polymer is greater when $x > 1$ than it was at the original, unaugmented incident light intensity, I_0. At depths greater than 4 μm the polymer degradation is less in the $x > 1$, $y = 1 + (\ln x)/(\ln 1.5)$ circumstances. Figure 2 displays $E_p/I_0 t$, the relative cumulative energy absorptions by the polymer to depth L, for the indicated x, y combinations. One notes that the cumulative energy absorptions by the polymer become less for the $x = 1.1$, 1.5, 2, and 3 instances than for $x = 1$ at approximately 10, 11, 13, and 18 μm depths, respectively. The relative cumulative energy absorptions, $E_p/I_0 t$, by the polymer to the characteristic depth L_c and to "infinite depth"

$$E_p/I_0 t = x k_p/\left(k_p + y k_a\right), \quad L \to \infty \qquad (7)$$

are listed in Table I for various x, y pair combinations based on the rule of thumb and its generalization.

Should the rule of thumb and its generalization be valid? If the failure mode which determines the useful lifetime of a given polymer product is sensitive to the amount of light absorbed by the polymer at the surface, or within a few microns of the surface, compensation for increased light intensity by increased UV absorber incorporation is not a viable approach. If, on the other hand, the lifetime is controlled by the total amount of light absorbed by the polymer to quite
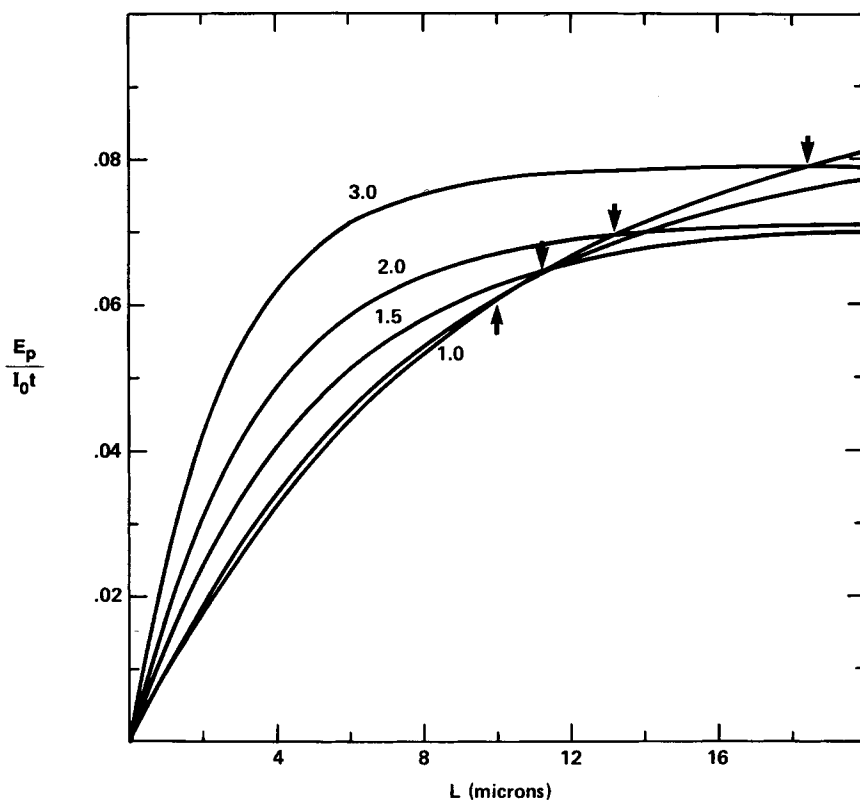
Fig. 2. Relative cumulative energy absorptions by the polymer as functions of depth for the systems described in the Figure 1 legend. The numbers on the curves are x. Arrows indicate the depths at which the cumulative energy absorptions by the polymer of the systems having $x > 1$ equal that of the $x = 1$ system.

TABLE I

Relative Energy Absorptions by the Polymer to the Characteristic Depth,
$L_c = 4.055 \, \mu$m and to "Infinite Depth" upon Irradiation
for t s by Light of Intensity xI_0[a]

		$E_p/I_0 t$	
x	y	To depth L_c	To infinite depth
1.0	1.000	0.0327	0.0909
1.1	1.235	0.0344	0.0824
1.2	1.450	0.0361	0.0774
1.3	1.647	0.0378	0.0744
1.4	1.830	0.0394	0.0725
1.5	2.000	0.0409	0.0714
2.0	2.710	0.0484	0.0712
2.5	3.260	0.0554	0.0744
3.0	3.710	0.0619	0.0788

[a]$k_p = 100$ cm^{-1}, $k_a = 1000$ cm^{-1}.

appreciable depths, the rule of thumb and its generalization have a reasonable basis. It would appear that the experiential base upon which the protection rule was established involved useful lifetime attributes more strongly dependent upon the total energy absorption by the polymer than upon the near-surface energy absorption by the polymer. The generalization by means of an assumed characteristic depth for equal lifetimes using the rule of thumb parameters $y = 2.00$ for $x = 1.50$ provides a decrease in the total light absorption by the polymer relative to that in the initial $y = 1$ for $x = 1$ situation. In an optically thick polymer product the greater degradation of the polymer near the surface as the light intensity is increased is therefore, in a sense, compensated by decreasing the total amount of polymer degradation.

Reference

1. A. R. Shultz, D. A. Gordon, and W. L. Hawkins, "Economic and Social Measures of Biologic and Climatic Change," CIAP Monograph 6, DOT-TST-75-56 Sept. 1975, 3.10 Materials Weathering, pp. 3-239–3-248.

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