Photodegradation of Rigid PVC Formulations. I. Wavelength Sensitivity to Light-Induced Yellowing by Monochromatic Light

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Synopsis

Light-induced yellowing of extruded rigid poly(vinyl chloride) formulations containing 0, 2.5, and 5 phr of titanium dioxide under exposure to monochromatic light was studied. Both photoyellowing and photobleaching were observed as wavelength-dependent phenomena in the range of 280–500 nm. Action spectra for yellowing of the different compounds were similar. In the case of the formulation with no titanium dioxide, significant color changes were observed on the back surface of the sample, indicating transmission of the longer wavelength light through the 1-mm thickness of the sample.

Light-induced degradation of poly(vinyl chloride), PVC, has been widely studied and the recent research reviewed by several workers.[1,2] The bulk of research literature on the subject is devoted to understanding the mechanism and the kinetic features of the photodegradation process. The experiments were typically carried out using solvent-cast virgin PVC resin films *in vacuo,* oxygen or nitrogen exposed to polychromatic light of wavelength > 254 nm.[3] A variety of techniques, including the measurement of hydrogen chloride evolution[4,5] and spectroscopy[3,6,7] has been used to monitor the photodegradation reactions.

While invaluable in understanding the basic photoreactions in pure PVC systems, the results from these studies cannot often be extended to the case of vinyl compositions commonly used in outdoor applications. The light-induced degradation of compounded, thermally processed poly(vinyl chloride), PVC, is a complex process. The various additives present in the formulation may absorb ultraviolet (UV) light (the virgin polymer is transparent to ultraviolet radiation) and affect the photodegradation of the polymer substrate by chemical interaction. Furthermore, the residual chromophores, mainly conjugated polyenes from thermal degradation while processing, also lead to the absorption of UV light by the material.[8] Chemical changes suffered by the additives themselves and the nature of products from such reactions are not even completely known for most formulations. Finally, the compounded rigid PVC formulations usually include titanium dioxide, TiO_2, as a light stabilizer.[9] The filler is known to be a pro-oxidant[10,11] but a good light screener,[12] and is widely used in extruded profile for outdoor applications.

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The present research relates to a rigid poly(vinyl chloride) formulation that is compounded and extruded into a ribbon. The samples are therefore similar to extruded profile (siding, window frames, etc.) where routine exposure to sunlight is an important consideration. In the case of white or light colored profiles, yellowing (or surface discoloration) is the initial result of prolonged weathering of a poor vinyl formulation.[13, 14] The extent of yellowing is therefore used to monitor photodegradation in the present work.

WAVELENGTH SENSITIVITY

While plastics in various applications are exposed to polychromatic light such as sunlight, it is important to understand the sensitivity of specific photoreactions to monochromatic light. Such data allow the identification of different wavelength regions in various polychromatic light sources that promote the undesirable degradation reactions. Knowledge of spectral sensitivities is also crucial in the design of ultraviolet light absorbers and filters for control of photodegradation.

Action spectrum refers to the relative sensitivity of a given reaction or a process to the wavelength of light. As such, the action spectra are specific to the material in question and depend on the criterion adopted to determine the extent of reaction (or the types of damage). Action spectra may be determined fairly conveniently using a source of monochromatic light. Ideally, the polymer (or other material) is exposed to identical photon fluence rates for a specific period of time and the extent of reaction determined using an appropriate technique, to yield the action spectrum. Thus the nature of the action spectrum depends on the absorption properties of the polymer, the efficiency of the photodegradation process, and the nature of the specific degradation process monitored.

In practice, a narrow band of radiation isolated from the dispersed spectrum of white light (usually from a xenon source) or a spectral line isolated from a suitable discrete spectrum (e.g., mercury vapor lamp) might be used. The photon fluence varies with wavelength, depending on the source, and the data need to be corrected for this factor. The ratio of the extent of reaction to the intensity is used in constructing the action spectrum, keeping in mind that the procedure does assume a linear dependence of the damage on intensity. Possible confusion of action spectra with intensity dependence has been pointed out in the literature.[15]

The present study was limited to an investigation of the action spectra for yellowing of a specific rigid vinyl formulation with and without added titanium dioxide. The ASTM yellowness index was used as the measure of degradation.

While yellowing index is by no means a sensitive indicator of early dehydrochlorination, at least in the case of PVC, it is important as a direct measure of visual discoloration of rigid vinyl surfaces on outdoor exposure.

YELLOWING OF PVC FORMULATIONS

Yellowing or discoloration of rigid PVC formulations readily occurs in inadequately stabilized compounds on extended weathering outdoors.[9, 13, 14] It is also observed with virgin PVC during photodegradation *in vacuo* or in

nitrogen.[4,7,15] The light-induced dehydrochlorination of the polymer creates sequences of conjugated double bonds which become progressively longer with the extent of reaction. These strongly absorb ultraviolet radiation. As the sequence length of the polyenes, n exceeds about 8, the absorption spreads into the visible region resulting in discoloration and yellowing.[7,16] While yellowing does take place in the presence of air or oxygen, it is relatively easier to induce photoyellowing *in vacuo* where there is no interference from the oxygen reacting with conjugate double bonds.[3]

Presence of titanium dioxide in the formulation stabilizes the PVC against yellowing, and the high reflectivity of the filler to visible light tends to mask any trace of yellowing that might be present as a result of processing.[9,13]

EXPERIMENTAL

Poly(vinyl chloride) Sample Preparation

A Georgia Gulf high-viscosity PVC resin was used in the fabrication of test samples. The compound used was generally similar to rigid vinyl formulations compounded for outdoor use in applications such as siding and extruded window frames, except for the titanium dioxide content. (Generally, 10–13 phr of titanium dioxide is used as a light stabilizer in outdoor formulations.) Three batches of the compound containing 0, 2.5, and 5 phr of rutile titanium dioxide, TiO_2, were used in the present study. The basic formulation used is given below.

The compounds were extruded at ~ 360°F in a single-screw extruder using a ribbon die and cut into 5×5 cm samples and stored in the dark under ambient temperature until exposure.

The PVC resin, compounding ingredients, and processing services were kindly provided by Georgia Gulf Corporation, Plaquemine, LA 70765.

Ingredient	Level
PVC resin	100.00
Organotin mercaptide	2.00
Acrylic processing aid	3.00
Modified acrylic impact modifier	6.00
Fatty acid soap	2.75
Amide wax	1.50
Calcium carbonate filler	10.00
Titanium dioxide	variable

The role of various compounding ingredients and the criteria for their selection have been discussed.[17]

Irradiation

Irradiation of samples was carried out at the Okazaki Large Spectrograph Facility (NIBB) in Okazaki, Japan. The large spectrograph used was equipped

with a 30 kW Xenon short-arc lamp with water-cooled electrodes. Radiation from this source was filtered through a distilled water filter to exclude heat and dispersed into a spectrum using a double-blazed plane grating with 1200 lines/mm. Monochromatic radiation of the desired wavelength was obtained by placing the samples at an appropriate position on a 10-meter long focal curve. A set of sharp cut-on filters was used to minimize the multiply diffracted light and other stray light reaching the sample position. Exposures were generally carried out at 23°C.

The equipment was calibrated using a mercury vapor lamp at the beginning of exposure. The stability of the source was continually monitored during the exposure experiments at preselected wavelengths. A long-term variation of about 2% in the fluence rate over a 10-h period was generally obtained with the system.

For exposures that required a condensed beam of higher intensity monochromatic light, the light at the focal plane was reflected via an appropriate 10×20-cm surface mirror through a 8.5-cm convex lens (quartz or glass). Temperature of the samples placed in the high-intensity beam was found to be generally the same as ambient (23°C) except in the case of the 400-nm and 500-nm beams where the sample temperature was about 25°C. The detailed description of the spectrograph and the instrumentation for measurement of photon fluence rates has been previously reported by Watanabe et al.[18]

Immediately after exposure, the samples were placed in black paper envelopes and stored at ambient temperature.

Yellowness Measurements

Yellowness measurements were carried out within 10 days of exposure using a Macbeth 1500 Colorimeter with an integrating sphere. The specular component of light was excluded and the ultraviolet portion included in the measurements. A white ceramic standard tile was used as the backing material. The ASTM yellowness index, calculated on the basis of the CIE standard illuminant C (CIE = 1931 2° standard observer viewing),[19] is expressed as

$$YI = \left[100\left(128x - 1.06z\right)\right]/y$$

where x, y, and z are tristimulus values of the sample with reference to source C. Several values of YI obtained from different parts of the sample were generally used to obtain an average value of the yellowness index. Reproducibility of the measurements with this technique is better than ± 0.25 units.

RESULTS AND DISCUSSION

The wavelength sensitivity of the compounded, extruded PVC material was determined by studying the change in the surface yellowness index on exposure to monochromatic light in the range of wavelengths 280 nm to 500 nm. Extended irradiation of the PVC results in the formation of progressively longer sequences of conjugated polyenes. Both the ability of the polyenes to absorb longer wavelength radiation[7,20] and the values of their extinction coefficient (which are generally quite large),[21] increase with sequence length.

Yellowing occurs only at moderate to high extents of dehydrochlorination. The rate at which visible yellowing develops depends upon several factors, such as the wavelength of radiation, residual chromophores in the starting material, the gaseous environment, the degree of plasticization of the PVC, etc.[8]

The samples used in the present study were thermally processed and therefore were essentially predegraded. A slight discoloration from chromophores introduced during processing (and possibly due to the presence of various compounding ingredients) was readily apparent in the initial samples (prior to exposure). Samples with no added titanium dioxide showed an average yellowness index of 21.8 while those with 2.5 phr and 5.0 phr of the filler gave values of 7.92 and 5.19, respectively.

Spectral Sensitivity

As shown in Table I, monochromatic light of wavelengths 280, 300, 320, and 340 nm resulted in yellowing of samples with and without added titanium dioxide. In agreement with the previously reported data,[21-27] the radiation of shorter wavelength yielded more severe yellowing degradation. Decker and Balandier[4] and others[25,26] have reported that radiation of wavelength > 300 nm does not result in significant dehydrochlorination of PVC. Under certain

TABLE I
Yellowness Indices of Extruded PVC Compound Samples Exposed to Monochromatic Light

TiO$_2$ phr	Wavelength (nm)	Total[a] Photons $\times 10^{-18}$	Colorimetry					Δ (Avg. YI[c])	YI/Total Photons $\times 10^{18}$
			L	a	b	YI[b](1)	YI(2)		
0	Control	0.00	89.62	−3.70	12.34	21.8	−	0	0
	280	34.56	87.58	−4.97	19.57	35.52	36.31	14.10	0.408
	300	58.32	87.89	−3.88	17.75	32.7	33.28	11.10	0.192
	320	82.08	89.29	−4.31	14.51	25.67	25.75	3.90	0.048
	340	112.32	89.43	−4.26	14.01	24.73	24.67	2.90	0.026
	400	112.32	90.21	−3.39	11.47	19.94	20.45	−1.60	−0.014
	500	166.32	90.37	−3.83	11.35	19.56	−	−2.20	−0.013
2.5	Control	0.00	94.89			7.92	−	0.00	0
	280	25.92	95.03	−1.72	5.61	9.49	9.51	1.58	0.061
	300	49.68	95.08	−1.43	4.91	8.37	8.43	0.48	9.66×10^{-3}
	320	79.92	95.17	−1.33	4.81	8.23	8.27	0.38	4.76×10^{-3}
	340	110.16	95.12	−1.31	4.70	8.07	8.07	0.18	1.63×10^{-3}
	400	103.68	95.20	1.24	4.45	7.69	7.69	−0.22	$−2.12 \times 10^{-3}$
	500	168.48	94.67	−1.36	4.28	7.42	7.42	−0.62	$−3.63 \times 10^{-3}$
5.0	Control	0.00	95.93	−0.95	3.03	5.19	−	0.00	0
	280	435	95.55	−1.82	5.72	9.57	−	4.38	0.01
	300	665	95.72	−1.20	3.69	6.26	−	1.07	1.61×10^{-3}
	320	956	96.01	−1.06	3.35	5.70	−	0.51	5.32×10^{-4}
	340	1078	96.60	−1.08	3.41	5.77	−	0.58	5.37×10^{-4}
	400	777	96.17	−0.88	2.95	5.10	−	−0.09	$−1.16 \times 10^{-4}$
	500	1520	95.81	−0.98	2.73	4.64	−	−0.05	$−3.62 \times 10^{-4}$

[a] Total photons per cm^2.
[b] YI is the ASTM yellowness index.
[c] Average change in ASTM yellowness index.

experimental conditions, such radiation results in mere rearrangements of polyene sequences and no further dehydrochlorination. Present data, however, demonstrate significant yellowing, and therefore dehydrochlorination, on exposure to light of wavelength $\lambda \leq 340$ nm.

The apparent disagreement between the two results arises due to the differences in the PVC materials used. Purified, solvent-cast films of PVC used in the earlier experiments probably did not contain the high concentration of residual polyenes, carbonyls, or peroxide groups typically found in thermally processed PVC such as that used in the present work. These functional moieties are powerful photosensitizers absorbing light of longer wavelength.[8] The presence of compounding ingredients in the polymer further modifies the present samples. (For instance, tin thermal stabilizers used in rigid PVC formulations are known[8] to accelerate the photooxidation reactions.) Containing a significant concentration of chromophores, the extruded samples are apparently able to absorb and use the longer wavelength radiation for dehydrochlorination. Lack of photoreaction at $\lambda \geq 300$ nm in previous studies is probably due to the lack of chromophores capable of absorbing in the wavelength range of interest. Predegradation of even the solvent-cast films by thermal treatment facilitates degradation by radiation of longer wavelength.[4]

In the case of polymers that are transparent to the ultraviolet spectral region of interest, the polymer itself has no inherent action spectrum. The light absorption process in materials such as PVC is solely dependent upon the presence of chromophoric impurities in the polymer. Thus, the observed action spectrum is characteristic of the nature and the concentration of chromophores initially present and would depend on both compounding and processing.

At 400 nm and 500 nm wavelengths, the samples underwent bleaching, reducing the yellowness index to values lower than the initial value obtained for unexposed samples. Table I shows the extent of bleaching observed for various samples. Photobleaching of PVC in the presence of air or oxygen has been previously discussed by several workers.[26,28,29] In fact, this competing reaction slows down the rate of yellowing of PVC compositions exposed to sunlight.[30] The bleaching process has been explained in terms of several mechanisms, including photoaddition of hydrogen chloride to polyenes resulting in reduced average sequence lengths in conjugated polyenes (and therefore in yellowing),[29,31] quenching of growing conjugate double-bond sequences by oxygen,[25,32-34] and reaction between oxygen and polyenyl radicals.[35] While the reaction of HCl with conjugated double bonds is the most plausible mechanism, it is likely that more than a single mechanism accounts for the process, as it takes place both in the presence and absence of oxygen,[29] in dark,[36,37] and, as a wavelength-dependent process, in light.[31] The quantum efficiency of photobleaching at 515 nm is significantly higher than that of the dehydrochlorination.[36] Since the bleaching reduces the concentration of long polyene sequences and therefore the amount of light absorbed by the polymer, PVC irradiated under oxygen tends to dehydrochlorinate at a slower rate than that under nitrogen.[38]

Figure 1 summarizes the behavior of various test samples in the yellowing region of the monochromatic action spectrum. To obtain information on the spectral sensitivity of the material to yellowing, the variations in intensity of
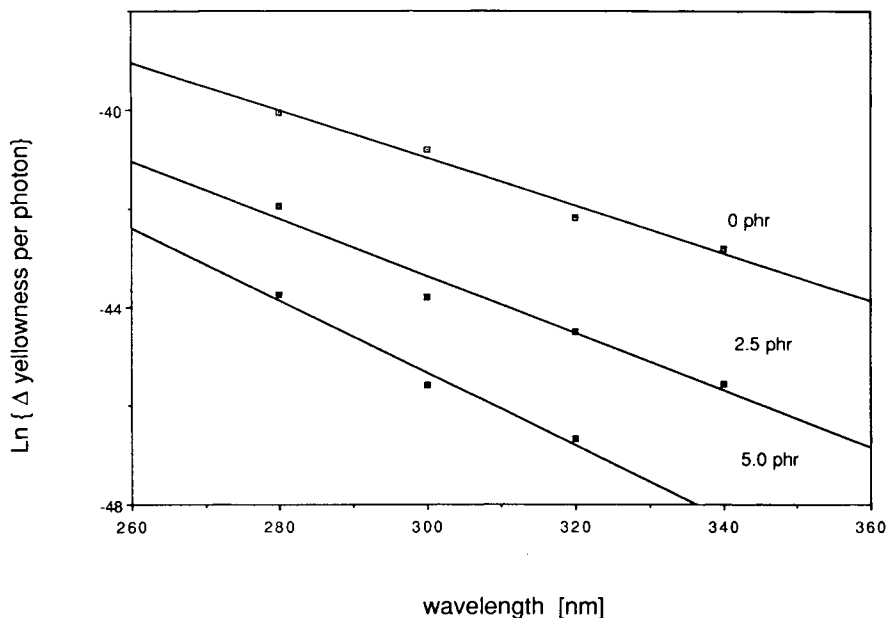
Fig. 1. Monochromatic action spectra for light-induced yellowing in rigid PVC formulations. phr: ☐ = 0; ▣ = 2.5; ■ = 5.0.

the light at different wavelengths need to be taken into account.[15] In the case of PVC, the fractional light absorbed by the polymer increases with the extent of photodegradation, as the conjugated polyene product itself is a photosensitizer. However, in spite of the severalfold increase in absorbance, the quantum yield of the hydrogen chloride generation apparently remains unaltered.[39] This suggests the rate of dehydrochlorination to be directly proportional to (approximately first order) intensity, as observed for specific wavelengths by several workers.[15,40] Normalization of data with respect to intensity assumes such linearity at all relevant wavelengths.

The plots in Figure 1 show the variation of Ln (change in yellowing/photons cm^{-2}) as a function of the irradiating wavelength. The plots show very good linearity (correlation coefficients of 0.98–0.99) and yield gradients which may be regarded as a measure of spectral sensitivity of the material to yellowing. The value of the constants a and $-b$ in the linear equation applicable to the data are:

$$
\begin{array}{llll}
0 \text{ phr TiO}_2 & a = -31.1 & b = 0.048 & r = 0.99 \\
2.5 \text{ phr TiO}_2 & a = -30.6 & b = 0.058 & r = 0.98 \\
5.0 \text{ phr TiO}_2 & a = -27.9 & b = 0.073 & r = 0.99
\end{array}
$$

The general form of the action spectrum and the approximate values of the gradients are not significantly affected by the presence of titanium dioxide.

The L parameter calculated ($L = 10 \ y^{1/2}$) from tristimulus values is a direct measure of lightness of the surface color, varying between zero (black) and 100 (white). The colorimetric data show a relatively small change in L, and significant variations of a and b, indicating that discoloration was not a
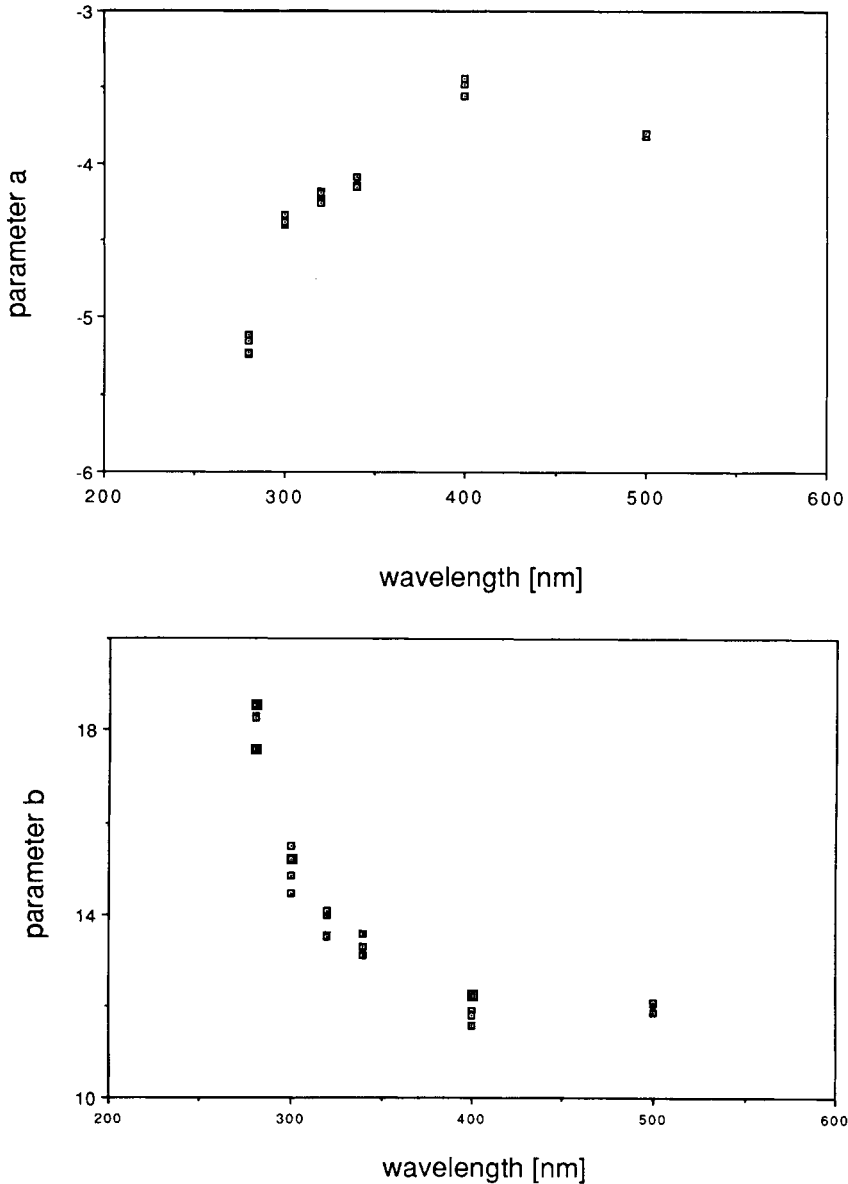
Fig. 2. Variation of parameters a and b with wavelength of exposure in yellowed rigid PVC formulation with no TiO_2.

mere change in lightness. Positive values of b indicate red/yellowness while the negative values of a correspond to a greenish hue. The starting material itself with $L = 89.51$, $a = -3.67$, and $b = 12.24$, for PVC without any TiO_2 may be described as a very light yellow-green surface. On exposure, the yellowness increases as seen by the change in b. The change in both a and b is shown as a function of the wavelength of exposure in Figure 2. It is clear that the change in these parameters is consistent with the visually observed
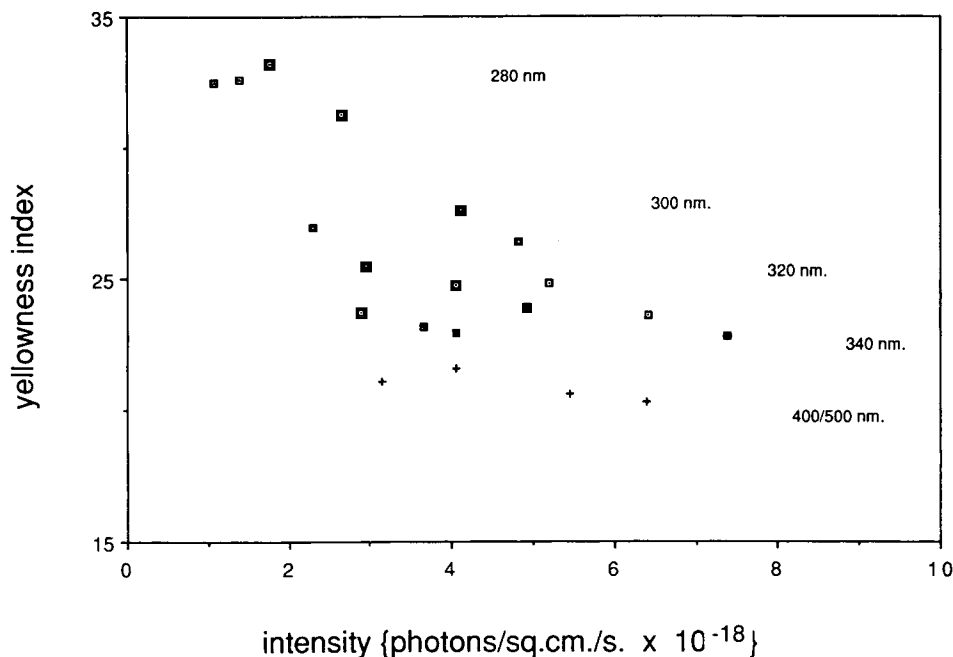
Fig. 3. Dependence of ASTM yellowness index on monochromatic light intensity at constant total exposure. nm: ▫ = 280; ■ = 330; ◙ = 320; ▩ = 340; + = 400–500.

development of yellowness and that the presence of titanium dioxide does not affect the variation. The latter observation is not surprising, as only the PVC material undergoes discoloration due to a similar chemical mechanism in both the presence and absence of the filler.

The intensity of light could be varied only to a limited extent using the present experimental set-up. By placing the samples at different areas of the monochromatic field of exposure, a severalfold variation in intensity was achieved. Exposing samples at different intensities of light (1.1×10^{15} to 9.5×10^{15} photons/cm^2/s $\times 10^{18}$) for various durations to obtain the same irradiance of 3.11×10^{19} photons/cm^2, followed by yellowness measurement, allowed a limited check of reciprocity in the case of samples with no titanium dioxide. As seen in Figure 3, the values of yellowness index did not show a dependence on the intensity.

Light Penetration

Yellowing of PVC compounds is usually a surface phenomenon,[41, 42] as the radiation is unable to penetrate the bulk of the sample due to the presence of titanium dioxide. The filler particles shield the polymer immediately below it from exposure absorbing the ultraviolet light falling on it. The quantitative aspects of light-shielding by fillers such as titanium dioxide has been discussed by Andrady and Shultz.[43] A comparison of the yellowness indices of the exposed and the reverse (back) surface of various samples containing at least 2.5 phr titanium dioxide with that of respective unexposed samples was
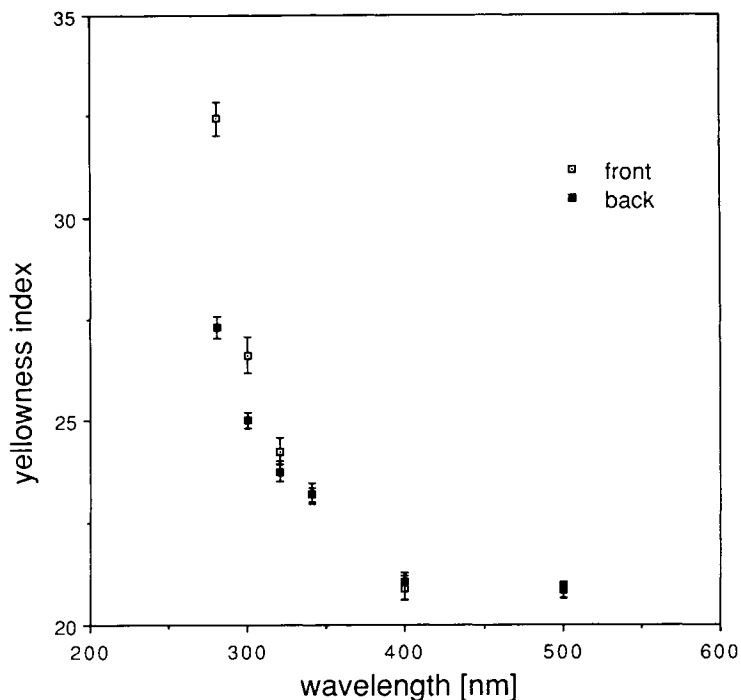
Fig. 4. Difference in yellowness indices between the top and bottom surfaces of rigid PVC formulation with no TiO$_2$, exposed to light of different wavelengths. ☐ = Front; ■ = back.

consistent with the above. The yellowness index of the reverse unexposed surface of all samples containing TiO$_2$ remained unaltered after exposure.

In the case of samples containing no titanium dioxide, however, evidence of light transmission through the 1-mm thick sample was obtained. As shown in Figure 4, the yellowness index of the unexposed surface significantly changed during exposure, presumably due to photoreaction caused by light transmitted through the sample. At least four samples per wavelength and two values of yellowness index measured at different areas on the sample surface were used in the experiment associated with the figure. The fractional transmittance would be wavelength dependent, with the shorter wavelengths more quickly attenuated in the polymer matrix. The shorter wavelength light in fact yielded less yellowing on the back surface compared to that on the exposed surface (a 25 to 50% reduction in the numerical value of the yellowness index). At wavelengths > 320 nm, both yellowing and bleaching at both surfaces were about the same for samples with no titanium dioxide.

The extent of yellowing within the bulk of the sample away from the surfaces was not determined in the present study. One possibility is that the yellowing and bleaching reactions will extend to a depth determined by the attenuation of the monochromatic radiation used. Especially in thick PVC sections the photoreaction in the bulk might be limited by the availability of oxygen or the lower concentrations of initiating chromophoric species. Feedosova et al.[44] reported such a phenomenon for natural weathering of PVC

compounds. The extent of the dehydrochlorination reaction was high at both surfaces but minimal within the bulk of the 1.5-mm sample.

CONCLUSIONS

The monochromatic action spectra for light-induced yellowing of a typical rigid vinyl compound, both with and without low extents of titanium dioxide light stabilizer, show a yellowing and a bleaching region. The former extends from 280 nm to about 340 nm for irradiation in air at 23°C, with the change in yellowness logarithmically decreasing with wavelength. The longer wavelengths 400 nm and 500 nm bleach the polymer under the same conditions and are likely to penetrate deeper into the polymer than the short wavelength light under ambient conditions. Thermally induced yellowing is readily bleached by the appropriate wavelengths of light. The spectral sensitivity of the bleaching process itself was not determined in the course of the current work.

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