

Photodegradation of Rigid PVC Formulations. III. Wavelength Sensitivity of the Photo-Yellowing Reaction in Processed PVC Formulations

Poorly formulated rigid poly(vinyl chloride) compositions undergo light-induced yellowing when exposed to sunlight for extended periods of time.¹⁻³ The prevention of uneven yellowing and subsequent chalking due to sunlight is an important consideration in the design of rigid PVC formulations for outdoor applications. To ensure adequate service lives, the compounds are generally protected with a light screener, rutile titanium dioxide. In spite of the slight prooxidant nature of the pigment,⁴ the addition of 10-13 phr of titanium dioxide (TiO₂) dramatically improves the light stability of PVC formulations.

Yellowing is essentially a consequence of the ready dehydrochlorination of polymer chains in the presence of light. Unlike the virgin resin, processed (normally extruded, in the case of rigid vinyl compositions) PVC compounds contain chromophoric impurities such as polyene sequences formed as a result of thermal degradation during processing.^{5,6} These moieties absorb short wavelength ultraviolet light, undergoing "zip" dehydrochlorination to yield long polyene sequences.^{7,8} When the sequence length of the polyenes exceeds about 8, visible yellowing of the vinyl results.⁹

Although the photodegradation process itself has been extensively studied, particularly in virgin polymer films,¹⁰⁻¹⁵ and to a limited extent in the processed PVC material,^{16,17} the wavelength sensitivity of the process has received little attention. Such information is useful in identifying the spectral regions which give rise to yellowing.

Wavelength sensitivity is directly measured by exposing the PVC compounds to monochromatic radiation, followed by a measurement of the change in yellowness. A high intensity white light source (such as a filtered xenon lamp) and a monochromator might be used to isolate the radiation of appropriate wavelengths. Alternatively, the beam of white light might be dispersed with a grating and the appropriate wavelengths isolated from the spectrum so obtained. In either case, the intensities of light obtained at different wavelengths will not be the same, as the source has a nonuniform spectral irradiance distribution. Thus, to compare the data at different wavelengths, it is necessary to calculate the change in yellowness per unit photon, assuming the change in yellowness to be a linear function of intensity in the range of intensities encountered. Although the dehydrochlorination reaction does suggest such a relationship,¹⁸ the linearity has not been demonstrated for the yellowing process. Alternatively, it is also possible to adjust the duration of exposure to each wavelength to obtain a constant total photon exposure at each wavelength. This avoids the need to correct the observed yellowness indices for intensity variations. If the linearity in fact applies, both experiments should yield similar results for the wavelength sensitivity.

The present work compares data obtained using the latter approach with published data for identical formulations generated using the former approach.

EXPERIMENTAL

The PVC formulation used was identical to that used in the previous study,¹⁹ and provided by Georgia Gulf Co. (PVC 100 phr, organotin mercaptide 2 phr, acrylic processing aid 3 phr, acrylic impact modifier 6 phr, fatty acid soap 2.75 phr, amide wax 1.5 phr, and calcium carbonate 10 phr). This compound is similar to those used in extruded rigid vinyl profiles, except for the lack of TiO₂. Titanium dioxide was not used in the formulation to ensure rapid photo-yellowing. Compound was extruded at 360°F in a single screw extruder in the form of a 2 mm thick ribbon and cut into samples approximately 5 × 5 cm.

Exposure to monochromatic light was carried out at Okazaki Large Spectrograph Laboratory in Okazaki, Japan. The features of the spectrograph have been previously discussed.²⁰ Equipment allows fully automated exposure of samples to variable intensities of monochromatic radiation.

TABLE I
 Yellowness Indices of PVC Samples Exposed to Monochromatic Light

Expt		Wavelength of irradiation (nm)					
		280	300	320	340	400	500
1	P	1.40	2.96	2.90	4.92	3.14	6.43
	T	6.17	2.91	2.97	1.75	2.75	1.34
	YI	32.68	25.50	23.74	23.89	21.11	21.00
2	P	1.08	2.31	4.05	3.67	4.05	4.42
	T	8.00	3.74	2.13	2.35	2.13	1.95
	YI	32.50	26.98	24.78	23.18	21.59	21.05
3	P	1.77	4.12	5.20	4.06	5.45	7.85
	T	4.88	2.09	1.66	2.13	1.58	1.10
	YI	33.24	27.60	24.83	22.94	20.61	21.13
4	P	2.66	4.82	6.42	7.38	6.39	9.46
	T	3.24	1.79	1.34	1.17	1.35	0.91
	YI	31.3	26.38	23.60	22.78	20.28	20.58
5 ^a	P	1.6	2.7	3.8	5.2	5.2	7.7
	T	6.00	6.00	6.00	6.00	6.00	6.00
	YI	35.92	32.99	25.71	24.70	20.20	19.56

^a Previously reported data.²² P [photons/cm²/s $\times 10^{15}$] is the photon fluence rate; T duration of exposure in hours, required to achieve exposure of 3.11×10^{19} photons/cm²; YI average ASTM yellowness index after irradiation (before irradiation the samples showed a YI = 21.80 units).

Yellowness was measured using a Macbeth 1500 colorimeter with an integrating sphere, excluding the specular component of reflected light. A white ceramic standard tile was used as the backing material and the ASTM yellowness index²¹ was calculated from the tristimulus values using the standard formula.²²

DISCUSSION

Of the six wavelengths studied, four (280, 300, 320, and 340 nm) resulted in an increase in yellowness index of the polymer samples. At the higher wavelengths of 400 and 500 nm, the samples underwent photobleaching resulting in a decrease in yellowness index. The samples were slightly yellow to begin with due to residual thermal degradation during processing and the presence of compounding ingredients. In compounds containing titanium dioxide, the initial yellowness is not readily apparent because of the high reflectivity of the pigment.

Table I shows the yellowness indices obtained at different intensities and different durations of exposure. The ASTM yellowness indices indicated are the average values from two or more readings from different areas of the sample. It is clear that the change in yellowness decreases with wavelength up to about 340 nm. As the total light energy per unit area available at each wavelength was constant (3.11×10^{19} photons/cm²), the values of yellowness index directly indicate the wavelength sensitivity. Using the data in the wavelength interval 280–340 nm, the wavelength sensitivity might be conveniently expressed as the gradient of the plot of \ln (change in yellowness index per photon per sq cm) vs. the wavelength. The plots (Fig. 1) yielded negative gradients of 0.036, 0.036, 0.032, and 0.042 (nm⁻¹).

The previously reported data (summarized in the table) were based on exposure for the same duration at different wavelengths, requiring the calculation of yellowing per photon per unit area, at different intensities of light assuming a linear dependence of yellowing on intensity. Value of the corresponding negative gradient so obtained was 0.048, a value not significantly different from the values obtained in the present work (t -statistic = -5.89 at 3 degrees of freedom $\alpha = 0.01$).

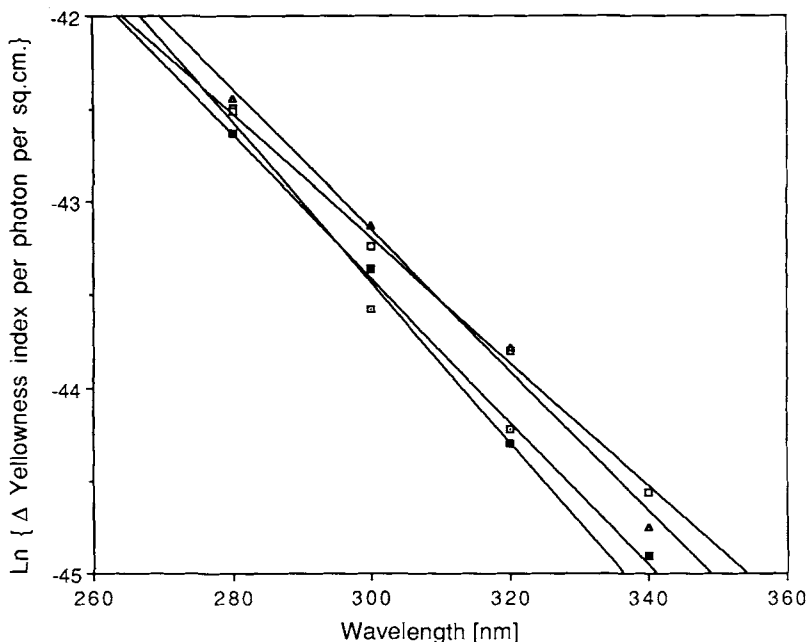


Fig. 1. Action spectra for yellowing of rigid PVC compound under monochromatic radiation. (■) data from Ref. 22; (other symbols) data from present work.

Present work demonstrates both experimental procedures to yield essentially the same result. At least in the intensity range indicated in Table I, a linear dependence of yellowing on light intensity (for the wavelengths studied) is suggested.

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