Photodegradation of Rigid PVC Formulations. II. Spectral Sensitivity to Light-Induced Yellowing by Polychromatic Light

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Synopsis

The wavelength sensitivity of a compounded extruded rigid poly(vinyl chloride) formulation to yellowing under exposure to filtered xenon radiation is determined using a cut-on filter technique. Spectral sensitivity of the formulation in the absence and the presence of 2.5 phr of rutile titanium dioxide was examined, and the results were compared to those previously reported for the yellowing of an identical vinyl formulation exposed to monochromatic light. Maximum in the activated spectrum for yellowing under exposure to filtered xenon radiation was found to be in the wavelength region 300–320 nm for both types of samples. The results agreed qualitatively with those previously obtained in the study of the same material exposed to monochromatic light.

INTRODUCTION

While the photodegradation of poly(vinyl chloride) (PVC) has been extensively studied[1-3] and reviewed recently by several workers,[4,5] the aspect of wavelength sensitivity has received relatively little attention in the research literature. Information on the wavelength sensitivity of polymers undergoing photodegradation is important not only to understand the spectral effects of different types of light sources, but also in the design of light stabilizer systems.

Hirt and Searle[6] reported the maximum extent of photoreaction in PVC homopolymer films exposed to a borosilicate glass-filtered xenon source to be due to wavelengths between about 310 and 325 nm. Changes in fluorescence and in ultraviolet, visible, and infrared absorption spectra were used as measures of photodegradation. Efforts by several others to identify the spectral response of PVC, based on these and different criteria of degradation including the generation of carbonyl functionality,[7] the evolution of HCl,[8] changes in the ultraviolet spectra,[9] and variation in the physical properties of the material[10] have been reported. However, in spite of their practical significance, very little data are available on the spectral sensitivity of compounded, extruded rigid PVC compositions, particularly those containing titanium dioxide. Rigid vinyl formulations are widely used in outdoor applications and are generally stabilized against photodegradation when pigmented with tita-

nium dioxide. The light-shielding effectiveness of titanium dioxide has been discussed by Andrady and Shultz.[11]

The presence of various compounding ingredients and their reaction products as well as the thermal history of processed PVC, directly affects the light sensitivity of the material. Scott et al.[12] discussed the effect of compounding ingredients on the light susceptibility of PVC. Thermal degradation during processing leads to the generation of several different chromophores such as conjugated unsaturation, peroxides, and carbonyl groups in the polymer.[13] The relative concentrations of the different chromophores depend on the specific formulation and on processing conditions.

Perhaps the most important consequence of exposure of PVC formulations to sunlight is the light-induced yellowing phenomenon. Whereas, the pure polymer does not absorb solar ultraviolet radiation, the compounded, processed polymer containing significant concentrations of chromophores is able to do so. Absorption of light results in "zip" dehydrochlorination of the polymer leading to the formation of conjugated polyene sequences.[2,14,15] Longer polyene sequences are able to absorb longer wavelengths of light and consequently lead to further dehydrochlorination of the polymer. When the sequence length exceeds about 5–8 units,[15,16] polyenes absorb blue light which results in yellowing of the material.

The spectral sensitivity of several compounded, extruded rigid PVC formulations to light-induced yellowing was previously reported.[17] This earlier study, employing a spectrographic technique, demonstrated light-induced yellowing of the material by several wavelengths in the region 280–340 nm. At longer wavelengths of 400 and 500 nm, the PVC formulations underwent photobleaching, possibly due to the destruction and/or rearrangement of the conjugated polyene sequences initially present. These results were generally consistent with previous observations[18] that photodehydrochlorination (which invariably leads to yellowing) is wavelength-dependent and occurs faster under exposure to shorter wavelength ultraviolet light. However, the broad range of wavelengths of 280–340 nm, within which yellowing, and therefore dehydrochlorination, was observed was not consistent with some reported data. For instance, Decker and Becker[19] and others,[20] reported that wavelengths longer than about 300 nm did not result in significant degradation leading to polyene formulation. Since PVC itself does not absorb ultraviolet light in the wavelength range of interest, 280–400 nm, and the photoinitiation is dependent upon the nature and the concentration of impurities and additives and on any thermal degradation products formed during processing, such discrepancies are to be expected.

The wavelength sensitivity for yellowing determined using a spectrographic technique identifies the dependence of the extent of yellowing on the wavelength of monochromatic light. Generally, the procedure involves exposure of the samples to narrow wavelength bands of light followed by measurement of the change in yellowness produced. The data, corrected for any differences in the intensities of the wavelength bands, yield the wavelength sensitivity or the action spectrum for photoyellowing of the material, which is independent of the light source. The correction procedure assumes a linear dependence of the extent of yellowing on the intensity of light. Such linearity has been reported for dehydrochlorination of PVC.[14] The uncorrected data are specific

to the light source used, and the plot is referred to as the activation spectrum.[21] It identifies the wavelengths in the light source which cause significant degradation of the material.

Similar information can also be obtained by means of the cut-on filter technique in which separate samples of the same material are exposed to the polychromatic light source behind each of the sharp cut filters in the set.[22] By a judicious selection of filters, the procedure allows indirect determination of the extent of yellowing due to narrow bands of the source spectrum. The data are used to plot the activation spectrum. In contrast to the spectrographic technique in which the effects of the spectral bands are determined in the absence of other radiation,[23] in the cut-on filter technique the samples are exposed to all wavelengths longer than the spectral band defined by each pair of filters. In this respect, the exposure conditions are closer to those of natural weathering in which the full spectral range of the source is incident on the samples. The relative extent of yellowing or other criteria of degradation due to the different spectral bands depends on the emission spectrum of the source. An action spectrum can also be generated from these data with the provisions stated above for conversion of one to the other.

Action spectra obtained using either technique depend on the absorption spectrum of the polymer, its susceptibility to the spectral energy absorbed, and the type of photoprocess monitored. The ability to absorb light is an obvious prerequisite for photodegradation. Since the wavelength dependencies of various photoreactions differ, the action spectrum often depends on the criterion of degradation used in its generation.

This study is aimed at determining the activation spectrum of a rigid PVC material undergoing yellowing under polychromatic light and the effect, if any, of the presence of titanium dioxide on the activation spectrum. Titanium dioxide is a particularly important pigment for rigid PVC formulations and its role in stabilization of PVC by its ultraviolet light screening capabilities is described elsewhere.[11,24] Yellowing of PVC is a particularly interesting study because the discoloration is complicated by the occurrence of a bleaching reaction[25,17] by longer wavelengths of light than those responsible for yellowing PVC. In sunlight both reactions evidently take place concurrently.

EXPERIMENTAL

Polymer Samples

A Georgia Gulf high viscosity poly(vinyl chloride) (PVC) resin was used for the fabrication of test samples. The resin, compounding ingredients and the processing services were kindly provided by the Georgia Gulf Corporation, Plaquemine, LA 70765.

The formulation used was similar to one that is typically used in extruded profiles intended for outdoor use, except that the titanium dioxide content was either 0 or 2.5 phr. Extruded profiles generally contain 10–13 phr of titanium dioxide pigment.[24] Residual thermal stabilizers in the formulation may also affect its photostability.[26] The material was extruded in a single screw extruder using a ribbon die and cut into test pieces approximately $5 \times 5 \times 0.1$ cm, and stored under ambient conditions in the dark until used.

The formulation is given below:

Ingredient	Level (phr)
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	0 or 2.5

The solvent-cast sample was prepared by casting from a dilute solution of tetrahydrofuran. The $\sim$ 5 μm thick samples were heated at 80°C *in vacuo* for 24 h before use. The absence of residual solvent in the film was established by infrared spectroscopy (absence of the 1060 cm^{-1} band in the IR spectrum).[27]

Light Exposure

The exposures were carried out in an Atlas 6500 watt borosilicate glass-filtered Xenon Weather-Ometer. A set of 17 cut-on filters for the wavelength range 266–473 nm (10% transmission) was used to determine the wavelengths responsible for the degradation. Tables I and II show the filter characteristics and indicate the pairs of filters used to define the relative effects of narrow bands of the source radiation. Figure 1(a) shows the ultraviolet transmission curves of five of the filters. The shift in the 40% transmittance values between adjacent filters in the series of cut-on filters is about 10 nm. Figure 1(b) illustrates the spectral band obtained by subtracting the transmittance of filter 6 from the transmittance of filter 5 at selected wavelengths. Similar spectral bands (spaced about 10 nm peak to peak) are obtained for the other pairs of filters in the series.

Each 2 × 2 in. filter was used for a separate PVC test piece of the same size, with the filter mounted about 1/8 in. from the front face of the specimen. The filtered specimens were backed with a piece of nonreflective black paper to prevent unfiltered light from irradiating the back side. They were exposed in standard sample racks to continuous radiation and were removed periodically to determine the yellowness index. Exposures were continued until the difference in the yellowness index of the pairs of test pieces exposed behind each pair of filters were large enough to yield a well defined activation spectrum.

Yellowness Index Measurement

Yellowness index (YI) was determined in accordance with ASTM D1925[28] by reflectance measurements using the Macbeth 1500 colorimeter with integrating sphere. The specimens were backed with a white ceramic standard reference tile. The ultraviolet component of the incident light was included and the specular component of the reflected light was excluded during measurement. The yellowness index was based on CIE standard illuminant D_{65} and CIE 1931 2° standard observer viewing. It was obtained from the tristimulus values X_{CIE}, Y_{CIE}, and Z_{CIE} relative to source C using the equation given below. The procedure is more completely described in

TABLE I
Filter Characteristics and Color Data for Unpigmented PVC Exposed 44 h to Xenon Arc Radiation behind Filters

Filter code	10% Trans. (nm)	Tristimulus values[a]			YI[b]	Filter pair	Band pass 20% trans. (nm)	Delta YI	Normal. factor	Delta YI (corr.)
		L	a	b						
2	266	71.5	6.4	19.8	55.9	2–3	272–293	2.1	1.11	2.3
3	282.5	73.2	5.4	19.9	53.8	3–4	286–304	4.1	1.09	4.5
4	296.5	74.8	4.7	18.9	49.7	4–5	298–319	11.0	0.88	9.7
5	306	80.8	1.9	16.7	38.7	5–6	308–327	7.8	1.11	8.7
6	315	81.4	2.2	13.2	30.9	6–7	317–340	5.6	0.88	4.9
7	324.5	85.6	−0.1	12.1	25.3					
8	331	87.4	−0.8	11.2	22.4	8–9	335–355	1.1	1.11	1.2
9	340	88.8	−1.7	11.2	21.3	9–11	344–367	0.9	0.88	0.8
11	355	88.2	−2.0	10.8	20.4	11–13	359–381	−0.4	1.01	−0.4
12	361.5	88.1	−0.5	9.8	19.7	12–14	366–391	−0.1	1.00	−0.1
13	363	87.3	−0.2	10.2	20.8					
14	370.5	87.6	−0.2	9.7	19.8	14–15	377–402	1.6	1.02	1.6
15	380	88.8	−0.6	9.2	18.2					
16	407	89.2	−1.2	9.1	17.4					
Unexposed		89.6	−3.7	12.2	21.5					

[a] Average of two measurements, each in a different area of the sample. The colorimetric coordinates are based on the Hunter L, a, b coordinate system: L is lightness ranging from 0 (black) to 100 (white); a indicates the degree of redness (positive a) or greenness (negative a); b indicates the degree of yellowness (positive b) or blueness (negative b).
[b] ASTM D1925 yellowness index.

TABLE II
Filter Characteristics and Color Data for TiO$_2$ Pigmented PVC (2.5 phr) Exposed 331 h to Xenon Arc Radiation behind Filters

Filter code	10% Trans. (nm)	Tristimulus values[a]			YI[b]	Filter pair	Band pass 20% trans. (nm)	Delta YI	Normal. factor	Delta YI (corr.)
		L	a	b						
2	266	79.3	1.8	24.5	56.9	2–3	272–293	2.9	1.09	3.2
3	282.5	79.9	0.6	23.7	54.0	3–4	286–304	8.1	1.07	8.7
4	296.5	83.5	−0.2	21.5	45.9	4–5	300–318	14.2	1.13	16.0
5	305	87.4	−1.1	15.9	31.7	5–6	308–329	−5.4	0.96	−5.2
6	315	85.9	−0.8	18.1	37.1	6–7	317–340	15.2	0.87	13.2
7	324.5	90.2	−1.5	11.6	21.9					
8	331	93.5	−1.1	6.5	11.9	8–9	335–355	5.9	1.09	6.4
9	340	94.6	−0.6	3.3	6.0	9–11	344–367	0.4	0.87	0.3
11	355	94.7	−0.6	3.0	5.6	11–13	359–381	0.0	1.00	0.0
12	361.5	94.7	−0.5	3.0	5.6	12–14	366–391	0.4	0.99	0.4
13	363	94.7	−0.5	3.0	5.5					
14	370.5	94.8	−0.5	2.8	5.2	14–15	377–402	−0.2	1.00	−0.2
15	380	95.0	−0.5	2.9	5.4					
16	407	95.3	−0.5	2.8	5.2					
Unexposed		95.0	−1.3	4.6	7.8					

[a] Average of two measurements, each in a different area of the sample. The colorimetric coordinates are based on the Hunter L, a, b coordinate system: L is lightness ranging from 0 (black) to 100 (white); a indicates the degree of redness (positive a) or greenness (negative a); b indicates the degree of yellowness (positive b) or blueness (negative b).
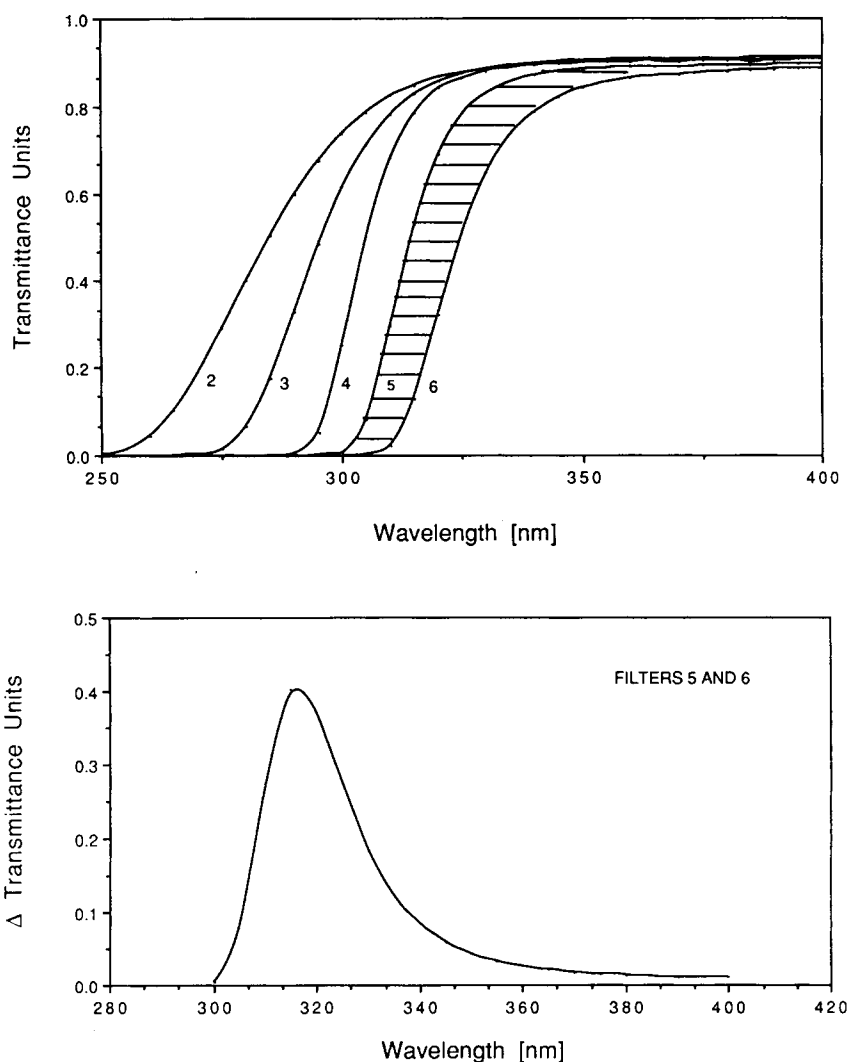[b] ASTM D1925 yellowness index.

Fig. 1.   (a) Transmittance characteristics of five cut-on filters used in the study. Filter code is given adjacent to the curves (see Tables I and II). (b) The difference in transmittance between filter 5 and filter 6 [i.e., the area shaded in Figure 1(a)].

ASTM D1925[28]:

$$YI = \left[100(1.28X_{CIE} - 1.06Z_{CIE})\right]Y_{CIE}$$

RESULTS AND DISCUSSION

In sunlight, the yellowing process brought about by short wavelength ultraviolet light is accompanied by a photobleaching reaction which is caused by light of longer wavelengths. Experimentally observed yellowing is therefore the net result of these concurrent competing processes. The process of the bleaching reaction has been explained in terms of several mechanisms includ-
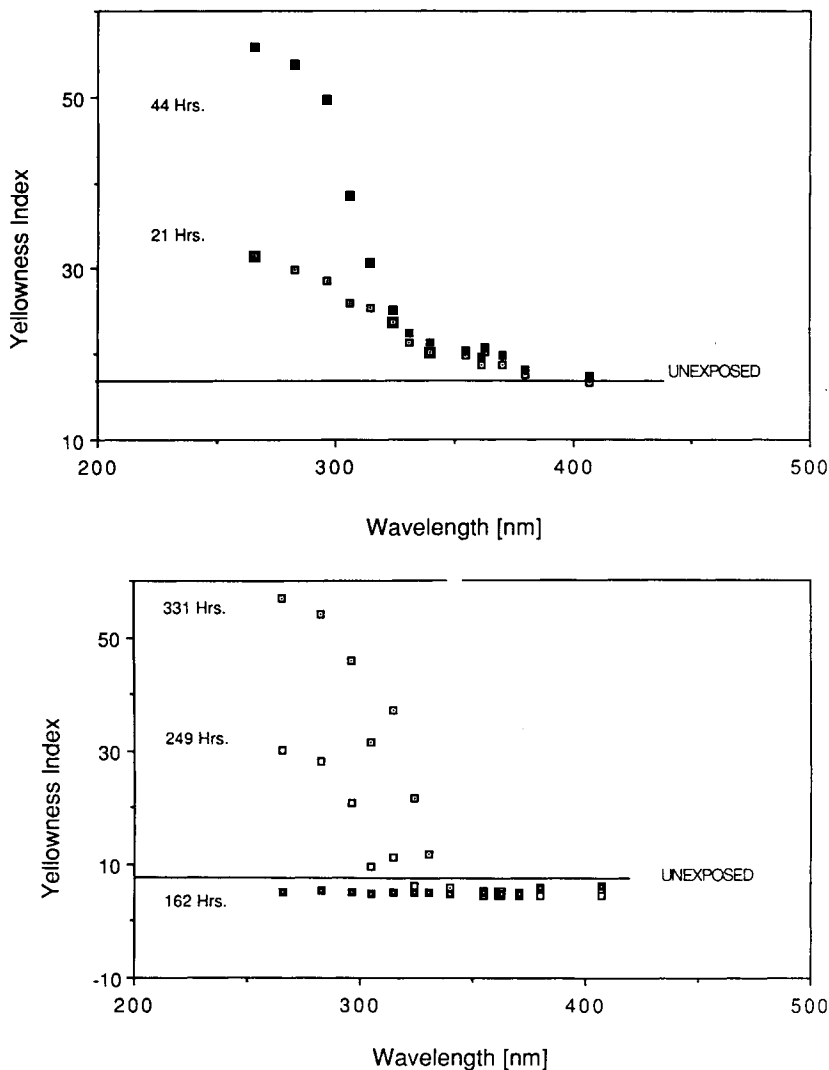
Fig. 2. The average ASTM yellowness index of the samples exposed behind the various cut-on filters at different durations of exposure to xenon radiation. The solid line indicates the average yellowness index of unexposed PVC samples. (a) Unpigmented PVC formulation; (b) PVC formulation containing 2.5 phr of rutile titanium dioxide.

ing photoaddition of hydrogen chloride to polyenes,[29] quenching of growing polyenyl radicals by oxygen,[30] and oxidation of polyene systems.[31] Yellowing under white light is observed when the polyene formation is the dominant process.

The average yellowness indices of unexposed samples containing 0 and 2.5 phr of titanium dioxide were 21.5 and 7.8, respectively. Figure 2 shows the yellowness index of these samples exposed to the xenon source for various periods behind the set of cut-on filters. The data for the 44 h exposure of unpigmented (0 phr TiO_2) PVC and for the 331 h exposure of pigmented (2.5 phr TiO_2) PVC are given in Tables I and II.
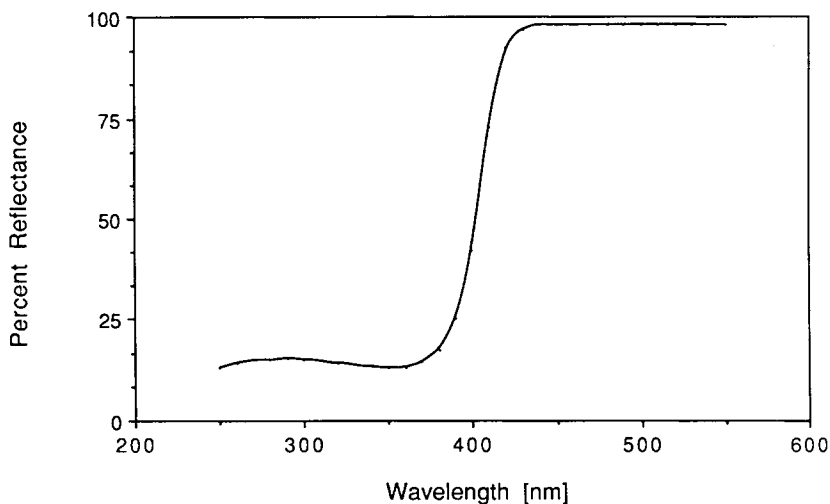
Fig. 3. Reflectance spectrum of rutile titanium dioxide powder in the ultraviolet-visible spectral region.

The unpigmented PVC samples underwent rapid photoyellowing when exposed to light including wavelengths shorter than about 330 nm yielding a measurable increase in yellowness index within 45 h of exposure. In contrast, those exposed only to wavelengths longer than about 410 nm exhibited photobleaching. The low initial yellowness of the samples due to degradation during thermal processing allowed the observation of the photobleaching process. In the wavelength range from about 330 to 400 nm, both processes probably occurred simultaneously,[25] but yellowing was dominant over the bleaching reaction. Figure 2(a) shows the yellowing obtained under different filters.

The pigmented samples containing 2.5 phr of titanium dioxide, however, underwent photobleaching behind all filters during the first 90 h of exposure. The presence of the pigment, which strongly absorbs the shorter wavelength radiation (see Fig. 3) responsible for yellowing and scatters the longer wavelength radiation, apparently suppresses the yellowing reaction during early exposure of these samples. Since the xenon source spectrum is similar to that of sunlight, it is very likely that the initial result of the outdoor exposure of processed PVC is also photobleaching. In spite of the ultraviolet light screening by the pigment, and the known high efficiency of the bleaching reaction,[32] on prolonged exposure yellowing was observed, particularly where the light included wavelengths shorter than 330 nm. The spectral sensitivity of the pigmented material beyond this "lag period" was not too different from that of the unpigmented material. Bleaching due to longer wavelength radiation was evident up to about 330 h of exposure behind filters. About 200 h of exposure without a filter was required in the case of the pigmented sample to attain about the same change in yellowness index as was attained by the unpigmented sample in 5 h of exposure.

The slower yellowing of pigmented PVC compared to that of unpigmented material on exposure to polychromatic light is expected merely on the basis of light absorption by the pigment. Furthermore, the surface of extrudate is

partially covered by highly reflecting pigment particles, which remain intact during exposure. Thus high levels of yellowing by the PVC resin domains are required to achieve even a moderate increase in the overall yellowness of the surface.

When the exposure is carried out in the presence of moisture, the possibility of pigment–water interaction to yield oxidants must also be considered. Studies on TiO_2/water systems suggest that hydrogen peroxide, OH radicals, etc. may be generated on exposure to light.[33] Even in trace concentrations such compounds are likely to cause effective photobleaching of yellowed PVC. In the present experiments where only low ambient humidity was available, such a process is regarded as unlikely.

In contrast to the compounded, processed PVC samples, the solvent cast film of the pure polymer did not show any yellowing under similar exposure conditions. No significant changes were detected in the ultraviolet–visible absorption spectrum of the film due to exposure. While a direct comparison cannot be made between the solvent cast and compounded/extruded samples because of the very large difference in the thicknesses of the samples (about 5 μm and 1 mm, respectively), it is clear that the pure homopolymer is relatively photostable. Lacking the chromophores introduced during processing (and/or those associated with additives), the pure resin is essentially transparent to ultraviolet light.

The activation spectra for yellowing of compounded and processed 1 mm thick PVC exposed to a xenon arc light source are shown in Figure 4. The data used to plot the activation spectra are given in Tables I and II. The maximum sensitivity of the samples with and without titanium dioxide is in the same range of wavelengths, about 300–320 nm. However, comparison of the activation spectra for the unpigmented (44 h) and pigmented PVC (331 h), both based on approximately the same increase in yellowness index, shows that wavelengths longer than 320 nm are relatively less effective in the pigmented material. The penetration of these longer wavelengths in PVC, which is normally greater than the penetration of the shorter wavelengths, is significantly reduced by the TiO_2.

The data show the particularly damaging effects of the short wavelength ultraviolet region of the spectrum, referred to as the UV-B region, in photoyellowing the PVC formulations under study. In view of the close similarity of the spectrum of sunlight to that of filtered xenon arc radiation in the ultraviolet region, the activation spectrum on exposure to sunlight is likely to be very close to that obtained using the xenon source. The data agree with that reported by Hirt and Searle[6] for 0.05 mm (2 mil) films of a commercial PVC homopolymer based on the spectrographic technique using borosilicate glass-filtered xenon radiation. The maximum of the activation spectrum determined in that study ranged from about 310 to 325 nm. It was also shown that 5 phr of TiO_2 had no effect on the activation spectrum.[34]

A study of the tristimulus values indicates that the observed changes in yellowness are due to a variation in ligthness as well as chromaticity. The L parameter, indicating lightness, slightly increased and parameters a and b generally decreased with increasing wavelength of irradiation in both sets of samples.

It is of interest to compare the wavelength sensitivity data reported for similar samples obtained using the spectrographic technique[17] with the above
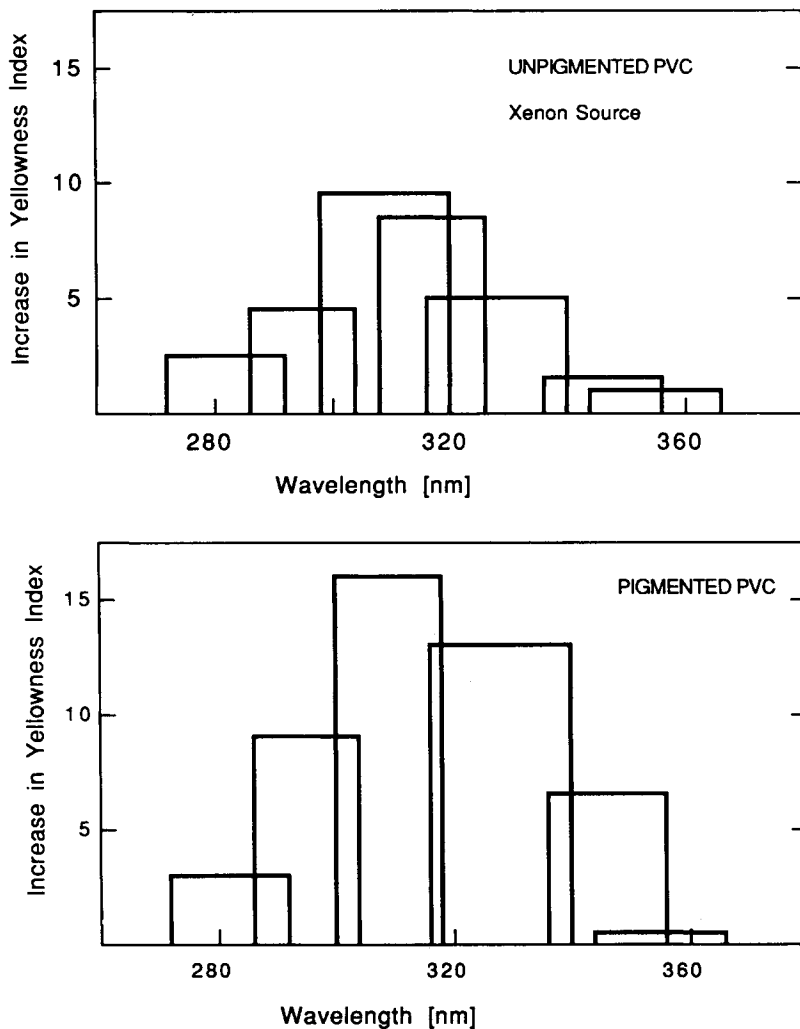
Fig. 4. Activation spectra for yellowing of compounded, extruded PVC material on exposure to filtered xenon light. (a) Unpigmented PVC formulation; (b) PVC formulation containing 2.5 phr of rutile titanium dioxide.

data. A convenient means of qualitative comparison is to use the spectral sensitivities previously reported by Andrady et al.,[17] $F(\lambda)$, as weighting factor for the appropriate irradiance of the filtered xenon source,* $H(\lambda)$, to obtain an

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*The irradiance data for a double borosilicate-filtered 6500 W xenon source in an Atlas Weather-Ometer were obtained from the manufacturer. The values (w/m²) for wavelengths of interest were as follows: 280 nm = 0.007, 300 nm = 0.043, 320 nm = 0.185, 340 nm = 0.350, 400 nm = 0.667 and 500 nm = 0.874. These were used as $H(\lambda)$. The $F(\lambda)$ values reported as change in average yellowness index for photon × 10¹⁸ in Ref. 17 are as follows:

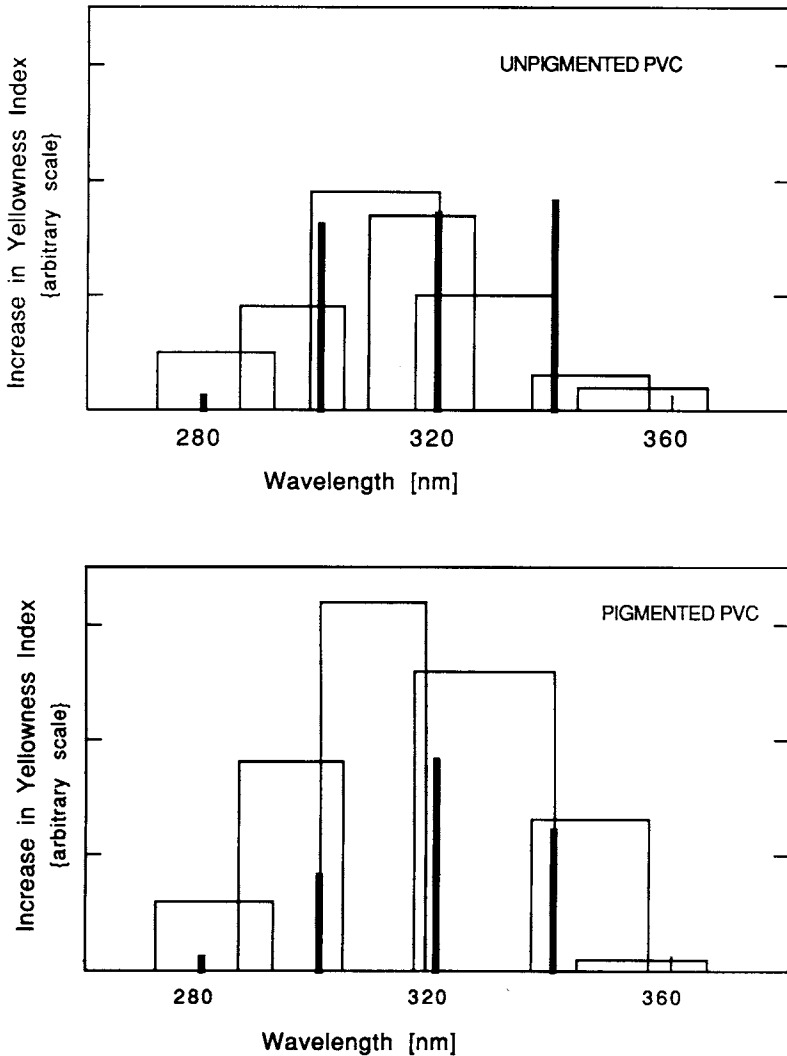| Wavelength (nm)	280	300	320	340
Unpigmented $F(\lambda)$	0.408	0.192	0.048	0.026
Pigmented (2.5 phr TiO₂) $F(\lambda)$	0.061	0.010	0.005	0.002

Fig. 5. Comparison of the shapes of experimentally observed activation spectra with those calculated from xenon spectral irradiance and published wavelength sensitivity data for similar PVC formulations. (a) PVC formulation containing 2.5 phr of rutile titanium dioxide; (b) unpigmented PVC formulation.

activation spectrum $F(\lambda)H(\lambda)$, which is specific to the xenon source. The spectra so obtained are comparable to those in Figure 4. The result of such a calculation for the wavelength region associated with yellowing is shown in Figure 5. The yellowness values are plotted on arbitrary scales for both sets of data to allow only the shape of pairs of curves to be compared. (The actual values of yellowness indices cannot be directly compared as the extent of exposure was different in each case.)

In the case of PVC with no titanium dioxide [Fig. 5(b)], the weighted monochromatic yellowing data suggest that the yellowing increases from 280 nm up to about 340 nm under filtered xenon light while the cut-on filter

technique shows an increase from 280 nm to about 310 nm and significantly less yellowing by wavelengths longer than 320 nm. The filter technique relies on exposure of samples to polychromatic light where the bleaching by long wavelength radiation occurs simultaneously with yellowing by the short wavelength light. Thus, while the test pieces behind the filters transmitting wavelengths longer than 320 nm receive radiation that is energetic enough to cause yellowing, the concurrent bleaching effect was apparently sufficient to significantly reduce the net discoloration. While the polyene species produced photochemically are probably also bleached during exposure, the bleaching that can be experimentally observed is limited to the initial yellowness of the sample.

The yellowing data for compounded PVC containing 2.5 phr of titanium dioxide are shown in Figure 5(a). The activation spectrum derived from monochromatic exposure data agrees well with that observed using the cut-on filter technique in the region of the spectrum where data were obtained by both techniques. The monochromatic spectral data at 340 nm weighted for the xenon irradiance at the wavelength yielded a yellowness value which was significantly different from the corresponding value at 320 nm.

CONCLUSIONS

Activation spectra of compounded, extruded rigid PVC based on the cut-on filter technique show that photochemical yellowing by a borosilicate glass-filtered xenon arc source is due largely to wavelengths between about 300 and 320 nm, both in unpigmented and pigmented PVC containing 2.5 phr titanium dioxide. Photobleaching by wavelengths longer than about 410 nm of the yellow species present in the processed material occurs during the initial periods of exposure. In the unpigmented PVC, yellowing by shorter wavelengths rapidly supersedes the bleaching reaction while in the TiO_2 pigmented PVC the rate of yellowing is reduced so that there is a significant "lag time" during which only photobleaching is evident.

The spectral sensitivity data in this study using the cut-on filter technique qualitatively agree with both calculated and experimentally determined activation spectra using the spectrographic technique. The calculated curve was based on a recent study of the action spectrum of identical material.[17] Both techniques show that wavelengths in the filtered xenon source longer than 300 nm and shorter than 340 nm are mainly responsible for yellowing PVC. It is postulated that the spectral sensitivity of PVC to sunlight is closely represented by these data.

References

1. J. F. Rabek, B. Ranby, and T. A. Skowronsky, *Macromolecules*, **18**, 1810 (1985).
2. E. D. Owen, in *Developments in Polymer Photochemistry*, N. S. Allen, Ed., Applied Science, London, 1982, p. 165.
3. D. Braun, *Pure Appl. Chem.*, **53**, 549 (1981)
4. W. H. Starnes, *Am. Chem. Soc., Symp. Ser.*, **151**, 197 (1981).

5. C. Decker, *Degradation and Stabilization of PVC*, E. D. Owen, Ed., Elsevier, New York, 1984.

6. R. C. Hirt and N. D. Searle, in *Weatherability of Plastic Materials*, Applied Polym. Symp. No. 4, M. R. Kamal, Ed. Wiley-Interscience, New York, 1967, p. 61–63.

7. K. G. Martin and R. I. Tilley, *Br. Polym. J.*, **3**, 36 (1979).

8. J. F. Rabek, T. A. Skowronsky, and B. Ranby, *Polymer*, **21**, 226 (1980).

9. R. F. Reinisch, *Am. Chem. Soc., Polym. Prepr.*, **7**(1), 372 (1966).

10. W. C. Warner and E. E. Gruber, *Ind. Eng. Chem., Prod. Res. Dev.*, **5**(3), 219–221 (1966).

11. A. L. Andrady and A. R. Shultz, *J. Polym. Sci.*, **33**, 1389 (1987).

12. G. Scott, M. Tahan, and J. Vyvoda, *Eur. Poly. J.*, **14**, 102 (1978).

13. G. Scott, M. Tahan, and J. Vyvoda, *Chem. Ind.*, **20**, 903 (1976).

14. D. Braun and S. Kull, *Angew. Macromol. Chem.*, **85**, 79 (1980).

15. V. D. Daniels and N. H. Rees, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2115 (1974).

16. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).

17. A. L. Andrady, K. Fueki, and A. Torikai, *J. Appl. Polym. Sci.*, (1988), to appear.

18. J. C. Marechal, *J. Macromol. Sci. Chem.*, **A12**(4), 609 (1978).

19. C. Decker and M. Balandier, *Eur. Polym. J.*, **18**, 1085 (1982).

20. W. H. Gibb and J. R. MacCullum, *Eur. Polym. J.*, **10**, 529 (1974).

21. R. C. Hirt and N. D. Searle, *Prepr. SPE RETEC*, 286–302 (1964).

22. N. D. Searle, in *International Conference on Advances in Stability and Controlled Degradation of Polymers*, A. V. Patsis, Ed., Technomic, Lancaster, PA, 1988, Vol. I.

23. N. Z. Searle, in *Analytical Photochemistry and Photochemical Analysis, Solids, Solutions and Polymers*, J. M. Fitzgerald, Ed., Dekker, New York, 1971, Chap. 9.

24. W. V. Titow, *PVC Technology*, 4th Ed., Elsevier, New York, 1984.

25. E. D. Owen and R. L. Reed, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2719 (1979).

26. J. F. Rabek, G. Canbach, and B. J. Ranby, *J. Appl. Polym. Sci.*, **21**, 2211 (1977).

27. J. Wypych, *PVC Degradation*, Elsevier, New York, 1985, p. 251.

28. *Annual Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia, 1988, Vol. 8.02.

29. E. D. Owen and J. Williams, *J. Polym. Sci. Chem. Ed.*, **12**, 1933 (1974).

30. J. F. Rabek, B. Ranby, B. Ostensson, and P. Flodin, *J. Appl. Polym. Sci.*, **24**, 2407 (1979).

31. J. M. Poochan, H. W. Gibson, and F. C. Bailey, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 447 (1980).

32. C. Decker and M. Balandier, *J. Photochem.*, **15**, 221 (1981).

33. N. S. Allen and J. F. McKellar, in *Photochemistry of Dyed and Pigmented Polymers*, Applied Science (London), 1980, p. 247.

34. N. D. Searle, unpublished data.