

## **Rapid Assessment of Weathering Stability from Exposure of Polymer Films. II. The Effectiveness of Different Regions of the Solar Spectrum in Degrading an ABS Terpolymer**

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### **Synopsis**

A simple and rapid method has been developed to determine the relative effectiveness of the different regions of the solar spectrum in weathering a polymer. The method is based on measuring the rate of degradation of the polymer in film form, exposed outdoors under a range of materials which transmit different amounts of solar UV. The stability of an unpigmented ABS terpolymer has been examined using this method. It has been shown that the relatively small amount of solar radiation in the range of 295-340 nm accounts for 41% of the total degradation process. Longer wavelengths are shown to be progressively less effective; wavelengths greater than 450 nm (which account for nearly 90% of the total energy of the solar spectrum) contribute less than 5% to the degradation process.

### **INTRODUCTION**

In protecting a polymer against weathering, it is important to know the relative effectiveness of the component parts of the solar spectrum in inducing chemical change in the polymer, i.e., to determine the activation spectrum for the degradation of the material with respect to the solar radiation reaching the Earth's surface. Work in this field has hitherto concentrated on the use of artificial light sources which approximate in the ultraviolet and visible region to the spectral distribution of solar radiation. The light from such sources is usually dispersed by a quartz prism<sup>1</sup> or separated into discrete bands by the use of filters.<sup>2</sup> Searle and Hirt,<sup>1</sup> using the former approach, have determined activation spectra by following changes in the UV absorption of polymeric materials as a function of wavelength. Other assessments of the degree of degradation, such as changes in the infrared absorption spectrum<sup>3</sup> and in tensile properties,<sup>4</sup> have also been used. The validity for outdoor weathering of the activation spectrum obtained from an artificial source will depend on the degree to which the spectrum of the source matches that of the time-averaged solar spectrum. The instantaneous solar spectrum is extremely variable, depending on the season, time of day, cloud cover, etc.<sup>5</sup> There is as yet no body of informa-

tion which includes the cumulative effect of such variables. Hence, how well the light sources used for artificial weathering correlate with the solar spectrum over considerable periods of time cannot yet be evaluated with confidence.

It has been shown that by applying sensitive nondestructive spectroscopic techniques to follow degradation of thin films, evaluation of a material can be completed in a few weeks. It should be possible to obtain the outdoor activation spectrum using readily available materials such as plate glass and poly(methylmethacrylate) as filters because their transmission characteristics remain substantially constant for the periods typical of film weathering trials.

It was decided to evaluate the filter technique by determining the activation spectrum of a typical poly(acrylonitrile-butadiene-styrene) (ABS) terpolymer. Detailed information on the weathering stability of some ABS terpolymers has recently been given,<sup>6</sup> but no information is available on the relative effectiveness of the different wavelengths of the time-averaged solar spectrum.

## EXPERIMENTAL

### Materials

The polymer studied was a nonpigmented commercial grade of ABS (percentage composition by weight acrylonitrile 23, butadiene 44, and styrene 33).

Films 10–15  $\mu\text{m}$  thick were cast from 10% (w/v) solutions in laboratory-grade chloroform and mounted in light alloy frames.

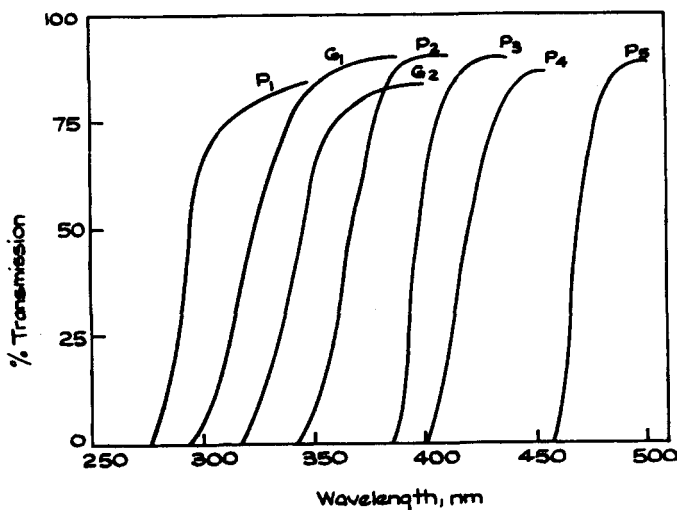


Fig. 1. UV transmission characteristics of materials used as filters: P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, etc. (various grades of Perspex) and G<sub>1</sub> and G<sub>2</sub> (glasses).

Seven materials were used as filters. Two were glasses,  $G_1$ , a 1-mm-thick microscope slide, and  $G_2$ , a 5.84-mm-thick plate glass. The other five materials were various grades of poly(methyl methacrylate) sheet supplied by ICI Ltd.:  $P_1$ , 3.2 mm clear Perspex CQ;  $P_2$ , 9.5 mm clear Perspex normal;  $P_3$ , 3.2 mm clear Perspex VA;  $P_4$ , 3.2 mm clear Perspex VE;  $P_5$ , 3.2 mm yellow Perspex 200. The transmission characteristics in the near-UV and visible region are shown in Figure 1.

### Exposure

Mounted films were exposed out of doors at ERDE at an angle of  $45^\circ$  to the horizontal facing South between February 22 and May 24, 1971. The surface of the filters was periodically cleaned with a damp, soft cloth.

Total solar radiation measured at the London Weather Centre, High Holborn (kindly supplied by the Meteorological Office, Bracknell, Berks.) was taken to apply to ERDE.

## RESULTS AND DISCUSSION

### Weathering of ABS Terypolymer Under Filters

The filtering characteristics of each filter material was unaffected by outdoor exposure over the complete trial period of four months; the final light transmission curve of each filter material was identical to that originally obtained.

As previously noted,<sup>6</sup> the main chemical changes resulting from the weathering of ABS materials are loss of unsaturation and growth of carbonyl and hydroxyl content. Because the relationship between these changes has been established, only the loss of *trans*-1,4 unsaturation, i.e., loss of infrared peak at 10.3 microns, will be reported here as a measure of degradation.

The changes in the *trans*-1,4 unsaturation content of films as a function of duration of exposure outdoors under different filters are shown in Figure 2. As previously pointed out, the variation of weather makes the time scale of Figure 2 an arbitrary measure of the integrated effects of the components of weathering—incident solar radiation has been found to be a more meaningful exposure parameter.

The total amount of solar energy (expressed as  $W\ h\ cm^{-2}$ ) incident on a polymer film is only slightly reduced by the introduction of the filters shown in Figure 1; they differ only in their transmission characteristics between 280 and 480 nm. The energy in this region of the solar spectrum constitutes only some 10% of the total solar radiation. For example, filter  $P_5$  transmits about 90% of the total incident solar radiation, while  $G_2$  transmits at least 97%.<sup>7</sup> Thus, it is valid to a first approximation to plot the  $\log_{10}$  (*trans*-1,4 unsaturation) against the same incident solar radiation energy for each film/filter combination. Figure 3 shows such a plot. It is seen that the initial period when no apparent chemical change occurs,

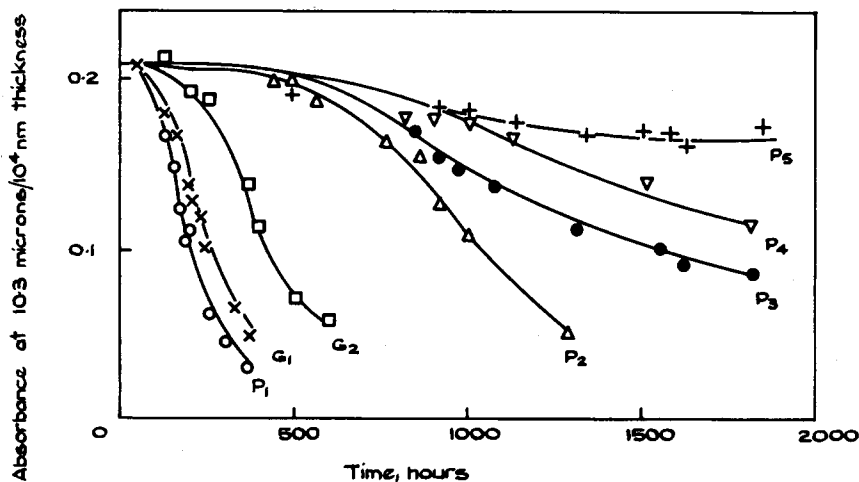


Fig. 2. *Trans*-1,4 unsaturation content of samples of ABS film exposed under different filters as a function of outdoor exposure time at ERDE.

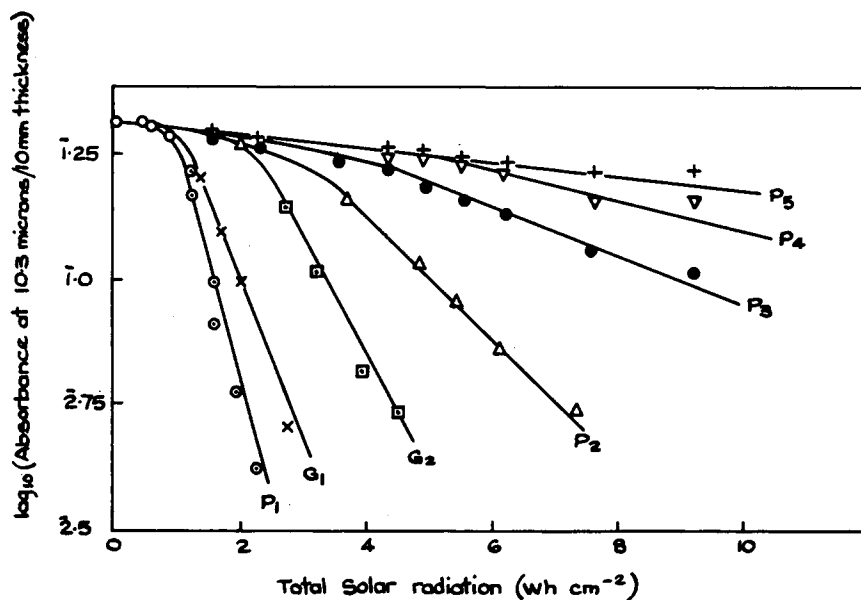


Fig. 3.  $\log_{10}$  (*trans*-1,4 unsaturation) of samples of ABS film exposed under different filters as a function of total solar radiation received.

termed the induction solar energy,<sup>6</sup> increases in the order  $P_1 < G_1 < G_2 < P_2 < P_3 < P_4 < P_5$ , and the subsequent degradation rates decrease in the order  $P_1 > G_1 > G_2 > P_2 > P_3 > P_4 > P_5$ .

The changes in the induction energies and in the rates of degradation indicate that while the total energy incident on the polymer under any of the filters differs little, there is a systematic diminution in *effectiveness* of the

TABLE I  
Contribution of Different Regions of Solar Spectrum to  
Degradation of ABS Terpolymer

Filter	Solar induction energy, W h cm <sup>-2</sup>	First-order rate constant <i>k</i> , cm <sup>2</sup> (W h) <sup>-1</sup>
P <sub>1</sub>	0.9	0.540
G <sub>1</sub>	1.4	0.320
G <sub>2</sub>	2.7	0.246
P <sub>2</sub>	3.5	0.128
P <sub>3</sub>	3.9	0.055
P <sub>4</sub>	5.5	0.039
P <sub>5</sub>	6.4	0.018

TABLE II  
Contribution of Different "Windows" of Solar Spectrum to Degradation of  
ABS Terpolymer

Light "window"	Wavelength range of "window," nm	Contribution to degradation reaction, %	Estimation of energy in "window" using results of Luckiesh <sup>8</sup>	Relative contribution to degradation for constant incident energy
(P <sub>1</sub> - G <sub>1</sub> )	290-345	41	4.3	245
(G <sub>1</sub> - G <sub>2</sub> )	300-390	13.5	11.8	29.4
(G <sub>2</sub> - P <sub>2</sub> )	335-390	21.8	19.6	28.4
(P <sub>2</sub> - P <sub>3</sub> )	350-410	13.5	31.0	11.3
(P <sub>3</sub> - P <sub>4</sub> )	395-450	3.0	30.2	2.58
(P <sub>4</sub> - P <sub>5</sub> )	405-500	3.9	101.6	1.0
(P <sub>5</sub> - ∞)	480-infrared	3.5	—	—

transmitted radiation in inducing degradation, which matches the effectiveness of the filters in screening out the UV content of the solar spectrum.

It has already been shown that the disappearance of the *trans*-1,4 unsaturation follows a first-order process<sup>6</sup> with respect to solar radiation. It is seen from Figure 3 that the disappearance of *trans*-1,4 unsaturation under each filter follows the same first-order process, i.e., a plot of log<sub>10</sub> (*trans*-1,4 unsaturation) against solar energy shows, after an induction solar energy, a linear relationship the slope of which is the first-order rate constant *k*. The induction solar energies and first-order rate constants determined from Figure 3 are shown in Table I.

The difference in transmission characteristics between adjacent pairs of filters is shown in Figure 4a. They can be considered as "windows" which are responsible for the difference in reaction rate between adjacent pairs of filters. If filter P<sub>1</sub> is considered to transmit the entire solar spectrum (albeit with some reduction in intensity because of reflection at the air/filter interface which, however, will be common to all filters), then the

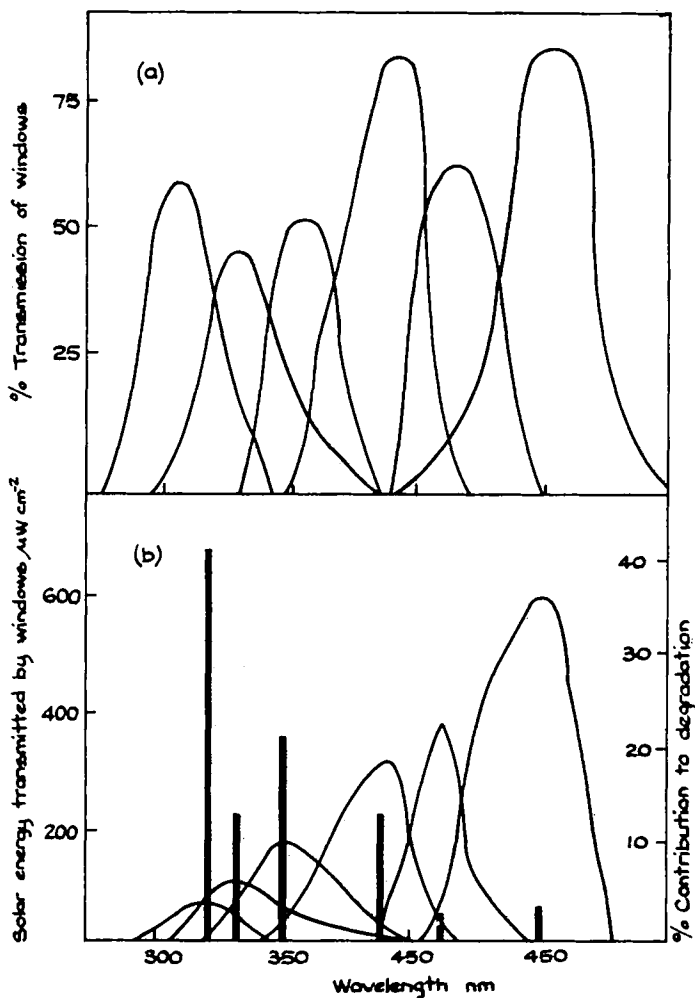


Fig. 4. (a) Transmission of light windows and their percentage contribution to the degradation process. (b) Estimated solar transmission of light windows using measurements of Luckiesh.<sup>8</sup>

percentage contribution of "window" ( $P_1 - G_1$ ) to the total reaction is given by

$$\frac{kP_1 - kG_1}{kP_1} \cdot 100$$

and that of "window" ( $G_1 - G_2$ ) by

$$\frac{kG_1 - kG_2}{kP_1} \cdot 100$$

and so on.

The contribution of each window is shown in Table II. It is seen that the window ( $P_1 - G_1$ ) containing the shortest wavelengths accounts for

nearly half of the total degradation. With increasing wavelength, the contribution to the degradation process decreases so that wavelengths above 400 account for less than 10%. An indication of the amount of solar energy transmitted by each window can be obtained by applying its transmission characteristics (Fig. 4a) to the solar spectrum data of Luckiesh.<sup>8</sup> The distribution so calculated for each window is shown in Figure 4b along with their contribution to the degradation reaction. The effectiveness of the shortest UV end of the solar spectrum in promoting photo-oxidation is even more pronounced if the relative contribution of each window is considered in terms of constant incident energy (Table II).

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