Rapid Assessment of Weathering Stability from Exposure of Polymer Films.   I. Real and Simulated Weathering of Commercial ABS Terpolymers

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Synopsis

Changes in the infrared transmission spectra of thin films were used to follow the natural and artificial weathering of ABS terpolymers.   Photo-oxidation of the polybutadiene moiety, which is the major process involved, occurs only after a well-defined amount of ultraviolet energy has been absorbed.   Thereafter, unsaturation decreases in a first-order manner with respect to UV energy absorbed.   Under artificial conditions with constant UV intensity, energy absorbed is synonymous with time, but this is not so in natural exposure because of the variability of solar energy and its UV content.   The method permits rapid comparison of commercial grades of ABS with the advantage of using natural conditions.   It has been shown that pigmentation (3.6 phr brown and 1.25 phr carbon black) increases weathering stability two- and fourfold respectively, as assessed by induction energy and rate of disappearance of unsaturation.

INTRODUCTION

It has been recognized[1] that a rapid means of comparing the weatherability of commercially available ABS plastics would be an advantage in choosing which of the wide and increasing range of grades is best suited to a given outdoor application.   It is obviously preferable, where possible, to make the comparison with reference to those properties[2,3] of practical importance; but the marked dependence of mechanical properties on test procedure and testpiece history unrelated to weathering introduces scatter into test results to such an extent that assessment of comparative stability is difficult, if not impossible.   One way of avoiding these difficulties has been to machine off the degraded surface and analyze it.[4]   Another is to examine the surface *in situ* by the infrared method of ATR (attenuated total reflection);[5] but this method is only semiquantitative.   Examining thin films by transmission spectroscopy[6] permits the course of degradation reactions to be followed without damage to, or interference with, the test area.   Furthermore, being nondestructive, it permits the same area to be used repeatedly for test, thus eliminating from the results the specimen-to-specimen variation inseparable from destructive test data.   In this paper, it will be shown that transmission infrared spectroscopy of thin films can be used to monitor the chemical changes arising in pigmented as well as

natural polymers and that quite short exposures to sunlight in temperate latitudes are sufficient to characterize durability.

EXPERIMENTAL

Materials

Table I lists the ABS materials used.   They were commercial materials from Uniroyal Ltd., with pigmentation to order incorporated by the supplier.   "Other matter" consists of soaps used in polymerization and antioxidant added during manufacture.

In addition to its being used as supplied, type 1 was used after extraction with methanol to remove "other matter" as described below.

Type 1 is a high temperature grade, type 2 is for sheet, and type 3 is a general-purpose injection-molding grade.

Films 10–15 μm thick were cast on glass from polymer solutions in dichloromethane and left until the solvent had evaporated.   The resultant dry films were floated from the glass with water and mounted on thin, light alloy frames with windows of 50 × 20 mm.   It was established that the presence of pigment particles did not materially affect the quality and resolution of either the infrared or ultraviolet spectra.   UV spectra for type 2
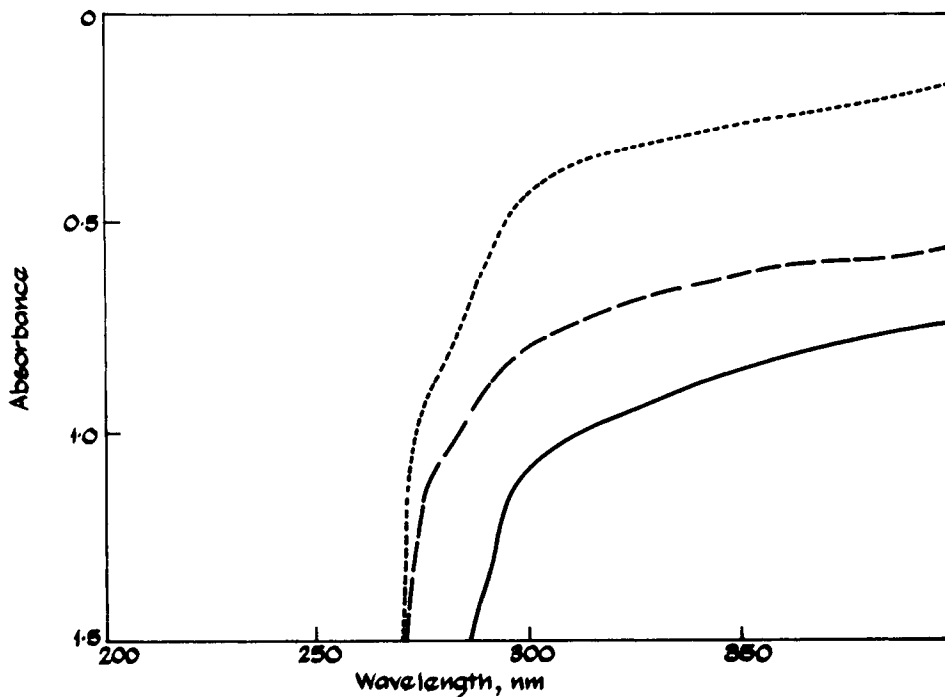

Fig. 1. UV spectra of pigmented ABS films (type 2): (.............) natural (13 μm thick); (-------------) brown (14 μm thick); (————) black (14 μm thick).

TABLE I
Composition of ABS Terpolymers

	Composition of polymer, % by weight				
Type	Acrylonitrile	Butadiene	Styrene	Other matter	Pigmentation, phr
1	20	25	52	3	None
2	22	43	32	3	None
					1.25 carbon black
					2.4 Cr_2O_3, 0.05 C black
					Cd yellow Fe_3O_4
3	22	36	39	3	None
					1.25 carbon black
					2.4 Cr_2O_3, 0.05 C black
					0.4 Cd yellow 0.8 Fe_3O_4

films in natural, brown, and black are reproduced in Figure 1; results for type 3 were similar. Films were exposed singly or in the form of a multilayer stack with the light passing the first film incident on the second, and so on.

Weathering Chamber

Specimens were exposed at 30°C in an environmental test chamber where the radiation source consists of 32 discharge lamps arranged on the circumference of a drum around which specimen holders rotate. An equal number of fluorescent lamps (TL20W/12) and black light lamps (TL-20W/08) from Philips Electrical Ltd. were used; their spectral energy distribution (as described by the supplier) is shown in Figure 2.

The light intensity of the exposure cabinet was measured by chemical actinometry using the potassium ferrioxalate method.[7] The intensity of a new set of lamps 40 mm from the lamps (the position of the specimens) was found to be 0.62×10^{14} quanta s^{-1} mm^{-2}. As the lamps aged, the light intensity decreased; after 15 and 52 hr, intensities were 0.54×10^{14} and 0.47×10^{14} quanta s^{-1} mm^{-2}, respectively. To minimize the effect of lamp aging, they were replaced in pairs at 100-hr intervals. Taking the incident radiation intensity on the front face of the sample as 100%, it was found that 18% of the light was reflected on to the back of specimens by the walls, etc., of the cabinet. Films were therefore exposed with an opaque back plate to eliminate this reflected light.

Outdoor Exposure

Mounted films were exposed outdoors at ERDE at an angle of 45° to the horizontal facing South, over the periods May 4 to June 3 and September 24 to 28, 1970. Total solar radiation measurements were taken from the records of the London Weather Centre (kindly supplied by the Meteorological Office, Bracknell, Berks) in view of its close proximity to ERDE (16 miles).
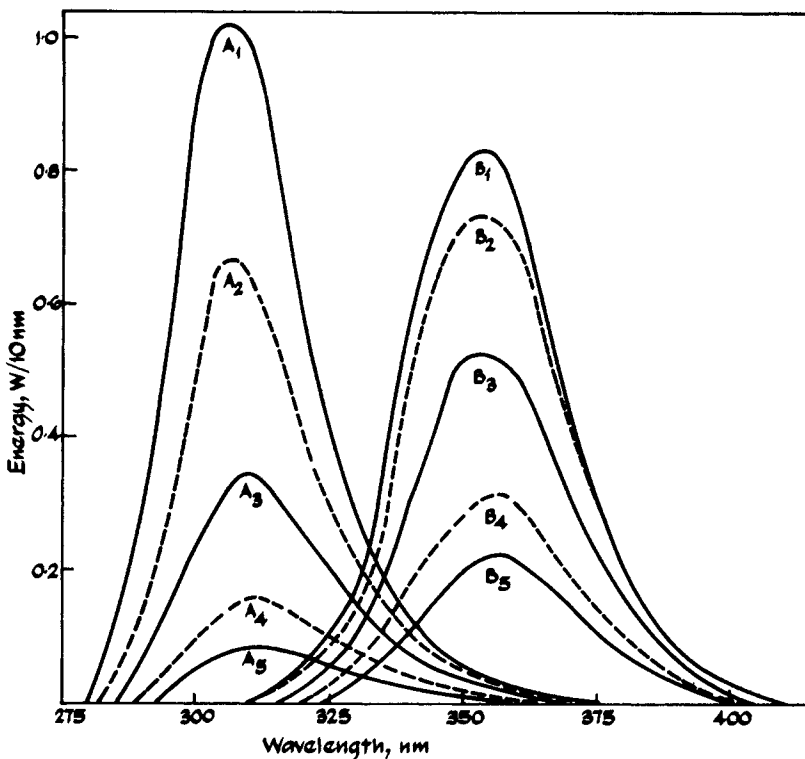
Fig. 2. A_1 and B_1 absolute spectral power distribution of lamps TL 20W/12 and TL 20W/08, respectively. A_2, A_3, A_4, and A_5 calculated absolute spectral power incident on polymer layers 2, 3, 4, and 5 due to lamp TL 20W/12. B_2, B_3, B_4, and B_5 same with respect to lamp TL20W/08.

RESULTS AND DISCUSSION

Infrared Spectrum of ABS Terpolymers

The infrared absorption spectrum of ABS has already been characterized.[6] The peaks at 4.45 and 13.2 μm have been assigned to the acrylonitrile and phenyl groups of styrene, respectively. The presence of 1,2 and trans-1,4 unsaturation is indicated by the peaks at 10.3 and 10.9 μm, respectively. Using the coefficients of Small[8] relating absorbances to group concentrations, it was found that the ratio of 1,2 to trans-1,4 unsaturation was 20:80 for all three types used. NMR measurements on carbon tetrachloride extracts of the terpolymers showed that the 1,4 unsaturation accounted for 81.5% of the total. There was thus little cis-1,4 unsaturation, the composition of the polybutadiene portion being approximately 81.5% trans-1,4 and 18.5% 1,2.

Artificial Weathering ABS

The acrylonitrile and styrene portions of the terpolymer (type 1 methanol extracted), as determined from the absorption bands at 4.45 and 13.2
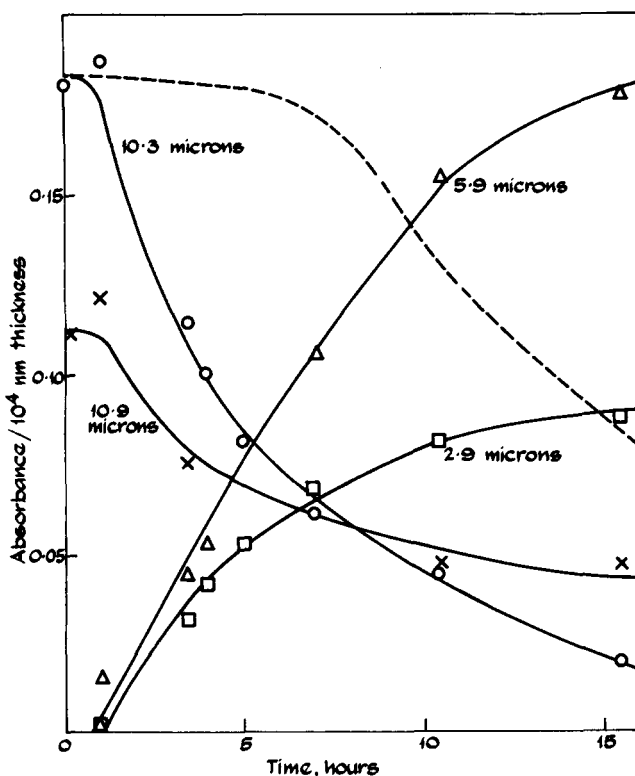
Fig. 3. Changes in *trans*-1,4 (⊙) and 1,2 (×) unsaturation, carbonyl (△), and hydroxyl (□) concentrations with time of exposure in Climatest of unstabilized ABS (type 1). Pecked curve refers to change in *trans*-1,4 unsaturation of stabilized ABS.

μm, respectively, were found to be unaffected by irradiation for 20 hr in the wavelength range of 300 to 400 nm, at a quantum intensity of 0.6 × 10^{14} quanta s^{-1} mm^{-2} (Fig. 2, curves A_1 and B_1). However, this exposure produced a marked decrease in the concentration of 1,2- and *trans*-1,4-butadiene unsaturation (Fig. 3), accompanied by the buildup of carbonyl and hydroxyl groups (infrared absorption peaks at 5.9 and 2.9 μm, respectively).

The absorbances at 10.3, 10.9, 2.9, and 5.9 μm after different periods of exposure are shown in Figure 3. There is an induction period of about 1 hr before the onset of degradation, probably caused by traces of stabilizer remaining after extraction. The unextracted ABS showed a much longer induction period (Fig. 3, pecked line).

The peak at 10.9 μm in ABS is not solely due to 1,2 unsaturation; it receives a contribution from a polystyrene peak. This is probably why prolonged exposure of ABS to UV radiation only partly reduces this peak (Fig. 3). Because of this complication, the 1,2 unsaturation was not considered quantitatively.
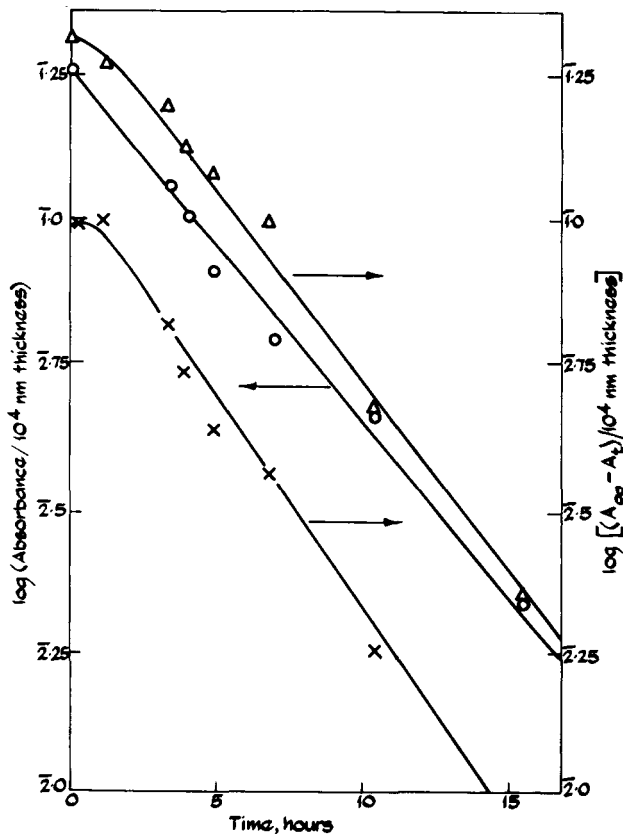
Fig. 4. First-order plot for ABS (type 1) exposed in Climatest: (⊙) disappearance of
trans-1,4 unsaturation; (△) and (×) buildup of hydroxyl and carbonyl concentration,
respectively.   In the two latter cases, A_∞ is maximum absorbance and A_t is absorbance
at time t.

Kinetics of Decrease of *trans*-1,4 Unsaturation and Increase of
Carbonyl and Hydroxyl

Under constant incident light intensity, *trans*-1,4 butadiene unsatura-
tion is destroyed at a rate proportional to its concentration, that is, by a
first-order process (Fig. 4).   Likewise, the growth of carbonyl and of
hydroxyl shows a similar relationship with time (Fig. 4).

Dependence of Degradation Rate on Light Intensity

To determine the dependence of degradation on light intensity, a stack
composed of five layers of ABS film was exposed in the weathering cham-
ber, and the concentration of *trans*-1,4 unsaturation for the different layers
was followed.

Each of the layers follows first-order kinetics for the disappearance of
trans-1,4 unsaturation (Fig. 5).   The linearity even for the layer furthest
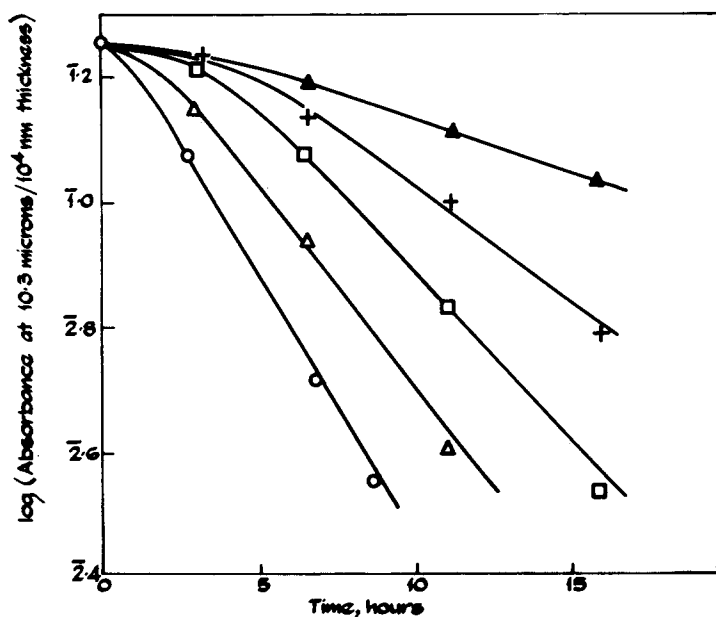from the source indicate that under these conditions no protective screen

Fig. 5. Exposure of sandwich composed of layers of ABS film (type 1). First-order plots for disappearance of *trans*-1,4-unsaturation for 1st layer (○); 2nd layer (△); 3rd layer (□); 4th layer (+); 5th layer (▲).

was formed by the growth of degradation products in the outer layers. This view was supported by the lack of changes in ultraviolet spectra of the film after more than 20 hr of exposure. The nonlinearity in the early stages of exposure of the inner layers is attributed to the presence of traces of antioxidant.

The UV transmission of the stack was measured for the first layer, the first plus the second, and so on, as a function of wavelength. From this information and the spectral distribution of the two types of lamps employed, the distribution of the light intensities incident on each layer can be obtained (Fig. 2). It is seen that while the intensity is decreased as it passes through successive layers of film, its distribution is not significantly altered. The relative intensities incident on each layer (obtained by measuring the total area under the appropriate pairs of curves in Fig. 2) plotted against the first-order rate constant for the disappearance of *trans*-1,4 unsaturation gives a straight line showing first-order dependence (and probably 1,2 unsaturation) on the light intensity (Fig. 6).

Evaluation of First-Order Rate Constant and Quantum Yield for *trans*-1,4-Unsaturation

As *trans*-1,4 unsaturation disappears by a first-order process with a rate constant proportional to the light intensity, the process may be expressed in the form
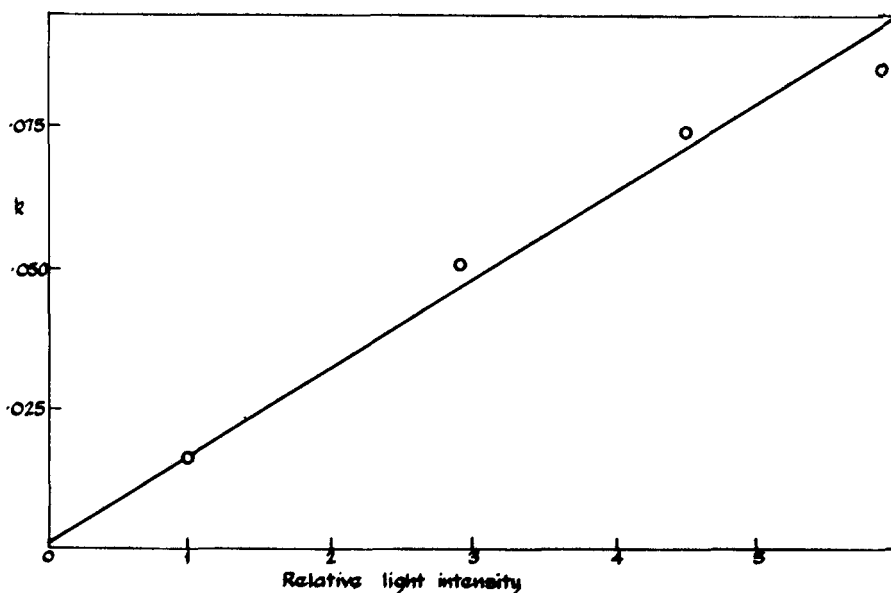
$$B_t = B_0 e^{-kIt} \tag{1}$$

Fig. 6. First-order rate constant k for the disappearance of *trans*-1,4 unsaturation of an ABS (type 1) as a function of relative light intensity in Climatest.

where k is the rate constant, B_0 is the original concentration of *trans*-1,4 unsaturated groups, and B_t is the concentration after exposure for time t during which light of intensity I is absorbed.

From Figure 1 it can be calculated that 20% of the measured incident light intensity (5.4×10^{14} quanta s^{-1} mm^{-2}) is absorbed; and from the results of Figure 3, k is calculated to be $3.3 \times 10^{-20} s^{-1}$.

The quantum yield of a photochemical process can be expressed as the amount of chemical change per quantum of radiation absorbed.   The *trans*-1,4 unsaturation falls from 2×10^{18} to 5.6×10^{17} molecular groups in 10 hr, thus giving a quantum yield of 0.04.   Hart and Matheson[9] found the quantum yield (as measured by the amount of oxygen absorbed by a polystyrene/butadiene rubber) varied from 0.16 at 313 nm to 0.016 at 366 nm.   Since the light source employed in this investigation was composed of lamps with peak emissions at 307 and 355 nm, it follows the quantum yield is of the same order as that found by Hart and Matheson and that approximately one unsaturated linkage is destroyed for each oxygen molecule consumed.

Natural Weathering of ABS

The changes in the IR spectrum of type 1 film exposed out of doors were qualitatively the same as those in films exposed in the environmental chamber.   The course of these changes in a film exposed outdoors at ERDE is shown in Figure 7.   A decrease in initial *trans*-1,4 unsaturation was not observed until the expiry of a fairly well-defined induction period
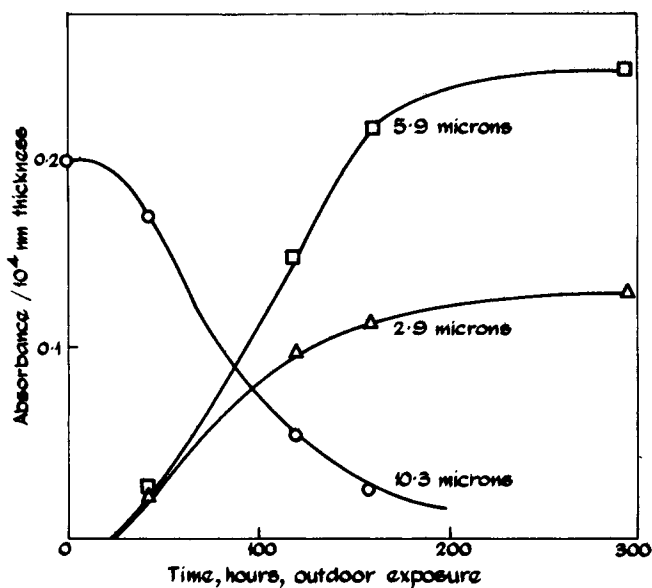
Fig. 7. Changes in *trans*-1,4 concentration with duration of exposure at ERDE of ABS (type 1): (○) *trans*-1,4 unsaturation; (△) hydroxyl (absorbance 2.9 μm); ▣ carbonyl (absorbance 59 μm).

which is attributable to the stabilizers which are present in all commercial ABS resins. After these stabilizers were consumed, the unsaturation decreased progressively with time of exposure and hydroxyl and carbonyl concentrations increased until no *trans*-1,4 unsaturation remained. This behavior indicates that it is the butadiene moiety of ABS which is vulnerable to photo-oxidation on outdoor exposure. The final values of the carbonyl and hydroxyl concentrations are very similar to those observed for samples exposed in the environmental test chamber and support the view that the same chemical processes occur in both environments.

Weathering of ABS as Function of Solar Radiation

Because of daily and seasonal variability of weathering conditions, the time scale on Figure 7 is an arbitrary measure of exposure. This variability is demonstrated in Figure 8 from which it will be seen that the degrees of degradation for three ABS films exposed for the same length of time, but at different periods, are not identical. Good agreement is obtained, however, if the degree of degradation is plotted against total solar radiation (Fig. 9). It has been shown that the photo-oxidation of polymers[10] is primarily dependent on the wavelength distribution and intensity of the UV portion of solar radiation and not on the total quantity of radiation received. The agreement of the curves in Figure 8 is probably a consequence of the three periods of exposure falling within a one-month period. During such a short span, it is likely that the UV content of the total solar radiation is approximately constant.[11]
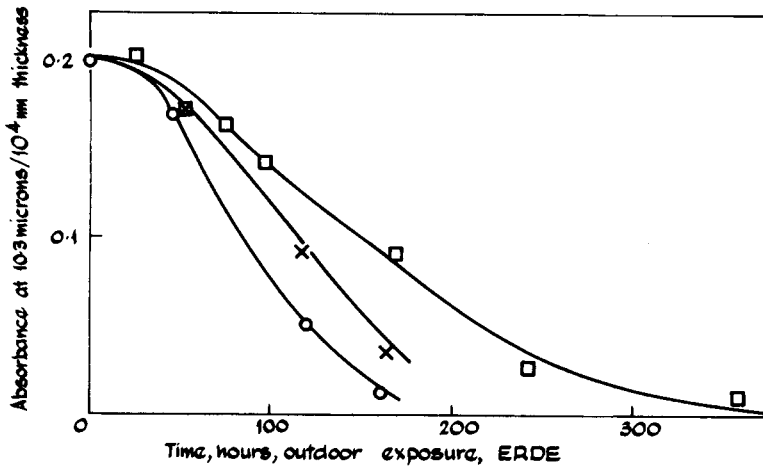
Fig. 8. Changes in *trans*-1,4 unsaturation content with duration of exposure at ERDE for three samples of the same ABS (type 1) exposed at different periods: (□) period beginning 4.5.70; (×) period beginning 22.5.70 (○) period beginning 3.6.70.
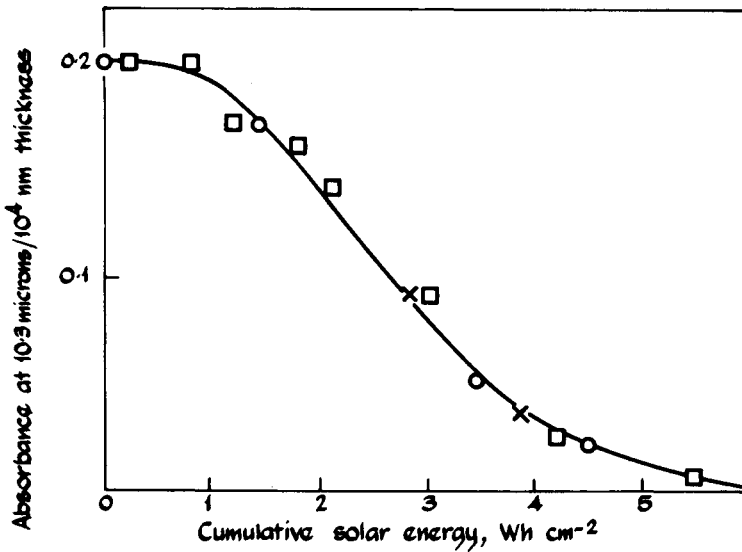

Fig. 9. Changes in *trans*-1,4 unsaturation content with total solar radiation received during exposure at ERDE for three samples of the same ABS (type 1) exposed at different periods: (□) period beginning 4.5.70; (×) period beginning 22.5.70; (○) period beginning 3.6.70.

Because of the variability in weather, it is more meaningful to express outdoor induction periods in terms of an induction solar energy (Fig. 10). After the induction solar energy, the loss of *trans*-1,4 unsaturation follows the first-order kinetic expression (1), with the modification that incident solar energy Σ (W h cm^{-2}) is substituted for t. The stability of different
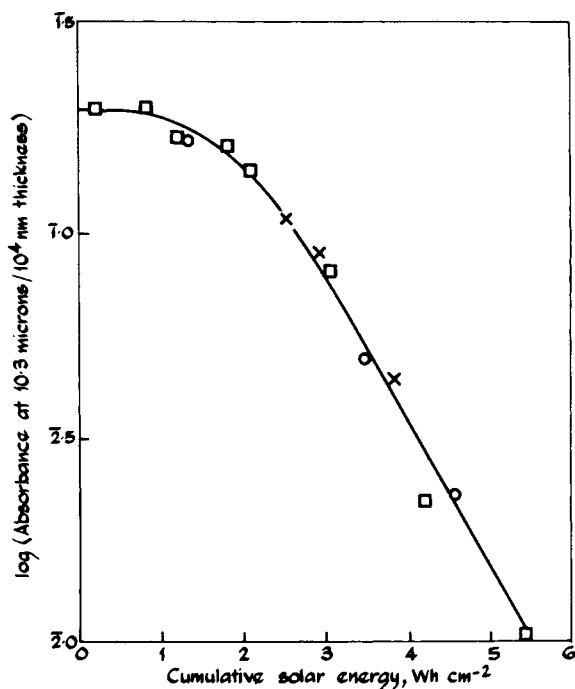
Fig. 10. Log-linear plot of change in *trans*-1,4 unsaturation content with total solar radiation received during exposure at ERDE for three samples of the same ABS (type 1) exposed at different periods: (□) period beginning 4.5.70; (×) period beginning 22.5.70; (○) period beginning 3.6.70.

ABS terpolymers to outdoor exposure can therefore be assessed by comparing their induction solar energies and first-order rate constants.

Outdoor Weathering of Pigmented Grades of ABS

The natural, brown, and black grades of types 2 and 3 show the characteristic fall in *trans*-1,4 unsaturation and growth of carbonyl and hydroxyl content when exposed outdoors for periods of less than ten days. As an example, the loss of *trans*-1,4 unsaturation for the type 2 resins as a function of incident solar radiation is shown in Figure 11. The induction solar energies and the first-order rate constants are given in Table II.

The induction solar energy for photo-oxidation of organic polymers has been shown to depend on the concentration, nature, and purity of the stabilizer or antioxidant present.[12] All six materials in Table II contain the same concentration of the same stabilizer (referred to the amount of base resin). However, since type 3 contains less polybutadiene than type 2 (Table I), the effective concentration of stabilizer is higher and probably accounts for the greater induction energies.

It is evident that while the values of first-order rate constants depend on pigmentation, there is little difference between the constants for type 2 and

TABLE II
Induction Solar Energies and First-Order Rate Constants

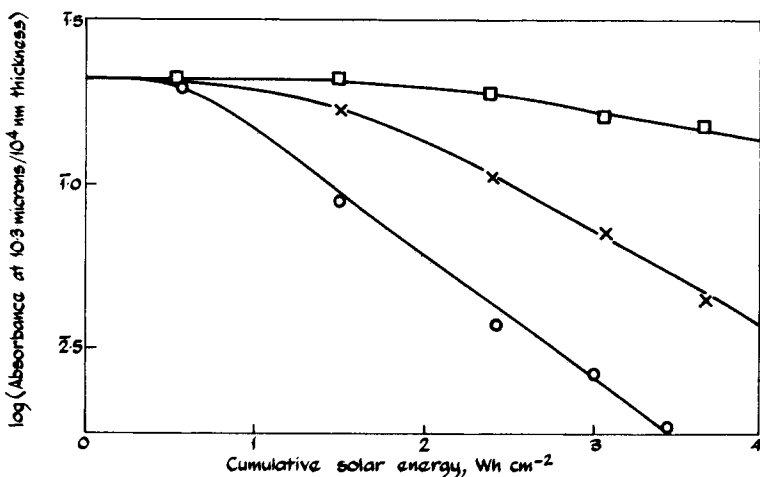| Type	Color	Induction solar energy, W h cm^{-2}	First-order rate constant, cm^2 (W h)$^{-1}$
2	Natural	0.5	0.80
	Brown	1.2	0.64
	Black	2.1	0.20
3	Natural	0.5	0.84
	Brown	1.5	0.59
	Black	2.3	0.16

Fig. 11. Log-linear plot of change in *trans*-1,4 unsaturation content of natural (⊙), brown (×), and black (□) ABS (type 2) with total solar radiation.

type 3 materials of the same color, in spite of differences of polybutadiene content.

The influence of the pigments in slowing the degradative process probably arises from their effect on the light transmission within the films. The UV transmission curves (Fig. 1) indicate that the order of absorbance between 290 and 400 nm (the range responsible for the photo-oxidation of polybutadiene[9]) is black > brown > natural. Light absorbed by the pigment particles is, presumably, not transferred to the polymer but is dissipated instead as sensible heat. The pigments may also have some chemical stabilizing ability, but it is likely that their prime roles are those of light absorbers and screens.

The corresponding ratios of reciprocal induction solar energies and rate constants for different ABS materials ranked by color are very similar (Table II). They indicate that the black material is some four to five times more stable than the natural and that the corresponding increase in stability between natural and brown is about twofold. Results of mechani-

cal tests on specimens from a current exposure trial on these materials will be examined to establish whether these ratios hold for changes in mechanical properties arising from weathering.

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