

Stabilization of ABS with Bound Synergistic Stabilizers Added as Masterbatches

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Synopsis

ABS masterbatch concentrates in antioxidants and UV stabilizers were added as conventional additives for normal ABS. The thermal and photo-oxidative performance of these polymers were compared with that of the commercial ABS and additives by measurement of carbonyl index and embrittlement times. From the result obtained, it is concluded that the addition of these additives in the form of masterbatches appears to be a better practical way of incorporating antioxidants and UV stabilizers into ABS simply by dilution of ABS, as these give thermal and light-stabilizing effects that cannot be achieved by stabilizers added in a conventional way. The bound stabilizers are resistant to leaching and chemical extraction.

INTRODUCTION

Although ABS has an excellent all-round combination as an engineering plastic, its outdoor performance is very poor, and therefore designs for outdoor must take account of its weatherability. In recent years, therefore, attempts have been focused on stabilization of ABS polymers against environmental degradation,^{1,2} chiefly thermal and photo-oxidation. To do this, antioxidants and UV stabilizers have been added to ABS. The conventional methods used are incorporation in the latex phase or copolymerization during synthesis or added during processing operations.

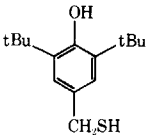
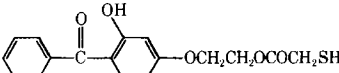
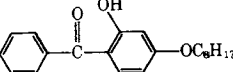
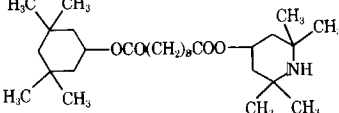
In the present work, an attempt has been made to improve the thermal and photo-oxidative performance of ABS by using antioxidant and UV stabilizers masterbatches as conventional additives for normal ABS. A high concentration of the antioxidant/UV stabilizer has been grafted onto ABS in the latex stage and the dry crumbs used as additives for stabilizing the mother polymer.

EXPERIMENTAL

Materials

The ABS used in this work was obtained by coagulating from the sample Cyclocac R 211 supplied by Borg-Warner. The ABS masterbatches—ABS(M₁) and ABS(M₂)—containing high concentration of 3,5-ditert-butyl-4-hydroxybenzylmercaptan (BHBM) and 4-benzoyl-3-hydroxyphenyl *O*-ethylthioglycollate (EBHPT), respectively, were prepared by grafting these antioxidant and UV stabilizers onto ABS in the latex phase. The commercial stabilizers used were UV 531 and Tinuvin 770. The stabilizers and antioxidants are listed in Table I with the code names used in this report.

TABLE I

	Code
	BIBM
	EBHPT
	UV 531
	Tinuvin 770

Grafting Procedure

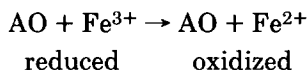
Before the grafting reaction was carried out, the ABS latex was stripped in order to reduce the concentration of the residual styrene monomer which would otherwise inhibit grafting. In the grafting reaction, a redox system was used. In this procedure, the emulsions of the antioxidant and UV stabilizers were maintained in aqueous suspension under high turbulence and brought into contact with the latex. The reaction was carried out at 57°C. The emulsions were purged with nitrogen before being added to the ABS latex which had been previously purged with nitrogen. Cumene hydroperoxide (pure) initiator was added in aliquots within the first half period of a reaction which lasted 5 h. At the end of the reaction, the ABS was coagulated using dilute acid and dried under vacuum at 45°C.

Extraction Procedure

The uncombined antioxidant and UV stabilizer materials were removed by continuous extraction of the crumbs with hot hexane in a Soxhlet apparatus. An extraction period of 48 h was found to be sufficient to remove all uncombined materials. After extraction, the polymer was dried under vacuum.

Quantitative Determination of Antioxidant/Stabilizers

The method used was based on that developed by Metcalf and Tomlinson.³ Essentially the method involves oxidation of antioxidant (AO) under controlled conditions using ferric ions:



In this reaction, the Fe^{2+} ions produced react with 2,2-bipyridyl to form colored complexes whose intensity is proportional to the concentration of the antioxidant.

An aliquot consisting of a suitable volume of extract was evaporated to dryness on a rotary evaporator. The extract was then dissolved in 5.0 cm³ toluene/ethanol mixture (25/75 v/v); 0.5 cm³ dipyrindyl solution and 1.0 cm³ Fe₂Cl₆/EtOH were then added. The mixture was shaken vigorously and transferred into a 10-cm³ volumetric flask. The aliquot vessel was washed out twice with toluene/ethanol mixture and the washing transferred to the volumetric flask, which was then made up to the volume with toluene/ethanol mixture. The flask was then allowed to stand in a bath thermostatted at 25 ± 0.1°C for 1 h. The absorbance was measured at 520 nm. The concentration of the antioxidant in the solution was obtained from a calibration curve constructed using BHBM solutions of known concentrations. It was found that up to 80% of the added antioxidant and stabilizers were bound to the polymer.

Processing

ABS with and without thermally stabilized masterbatch [ABS(M₁)] was mixed in the RAPRA torque rheometer model MK 3 for 3 min at 190°C at high speed and a ram pressure of 40 psi. Varying concentrations of ABS(M₁) were added to normal ABS. The samples were processed with closed chambers. The hot melt was quickly removed from the chamber and rapidly cooled in cold water. Normal ABS was also mixed with the masterbatch containing UV stabilizer [ABS(M₂)] and processed under similar conditions as the proceeding samples. Also a combination of ABS(M₁) and ABS(M₂) at various ratios was added to normal ABS and processed as before. The conventional commercial stabilizers UV 531 and Tinuvin 770 were similarly added and processed.

Pressing of Films

Four specimens of 0.5 g each were placed between the glazing plates between cellophane paper. They were preheated in the press at 190°C for 1½ min without pressure. They were then pressed at 60 psi pressure for another 1½ min. These gave the required thin films of thickness between 0.0025 and 0.003 in.

Testing

The measurement of carbonyl, hydroxyl, and *trans*-1,4-polybutadiene absorbance was carried out using Perkin-Elmer model 457 infrared spectrophotometer.

Irradiation Procedure. Accelerated indoor weathering of ABS films was carried out in a UV cabinet supplied by Laboratory Thermal Equipment Limited. This sunlight-blacklight machine deliver constant spectra characteristically approximately that of sunlight. The degradation was followed by running IR spectra of the films at regular time intervals. Temperature inside the cabinet was about 30°C.

Heating Procedure. Accelerated thermal oxidation of ABS films was carried out by mounting the sample films on specially prepared cardboard holders and suspended with copper wires in the cavity of the Wallace air oven at 100°C. Each sample film was contained in a separate cavity. The degradation was then followed by running the IR spectra at regular intervals of time.

Procedure for Measuring Embrittlement Times. The specimens were tested for embrittlement at regular time intervals. The test was carried out by bending the specimen twice at 180°C. The first bending was performed toward the irradiated surface, and the second was carried out by bending toward the unirradiated surface. This was a severe test for polymer films.

Results and Discussion

The stability of ABS toward accelerated environmental degradation was studied by two methods: photostability and thermal stability. In these studies, the growing or diminishing bands centered around the double bands at 965 and 912 cm^{-1} , the ketonic band around 1720 cm^{-1} , and the hydroxyl band around 3500–3400 cm^{-1} were followed.

Photo-Oxidation of ABS

Figure 1 shows the dependence of functional group indices upon UV exposure with time for an unstabilized ABS. The figure shows a small induction period for all the functional groups. At the end of the induction periods, the —OH and C=O group indices increase quite rapidly with time, while the —C=C— index falls. The photodegradation has also been shown to proceed by a first-order reaction.⁴ In addition, a measure of loss of impact strength follows the same pattern as the degradation of the C=C bonds.⁴ These suggest the destruction of the double bonds.

Figures 2–5 are plots of various functional indices as a function of exposure time. Figure 2 represents a characteristic graph for the photo-oxidation of ABS containing ABS(M₂). Altogether four concentrations of masterbatches to give different amounts of bound UV stabilizer were added to normal ABS, as shown

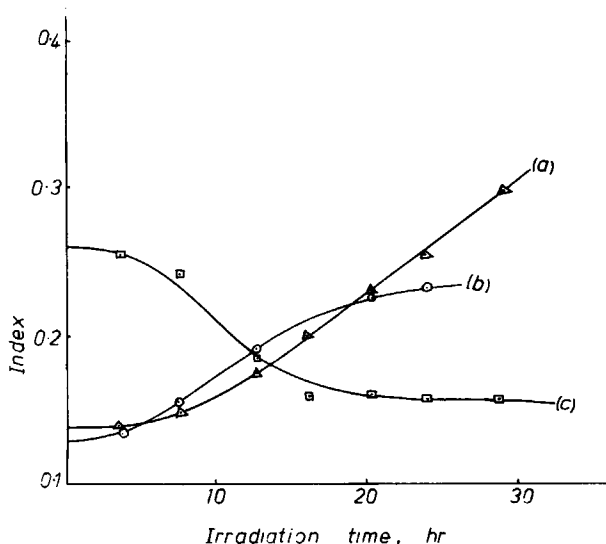


Fig. 1. Photo-oxidation of ABS. Dependence of functional group indices on time upon UV irradiation of unstabilized ABS: (a) carbonyl index; (b) hydroxyl index; (c) carbon-carbon bond at 965 cm^{-1} .

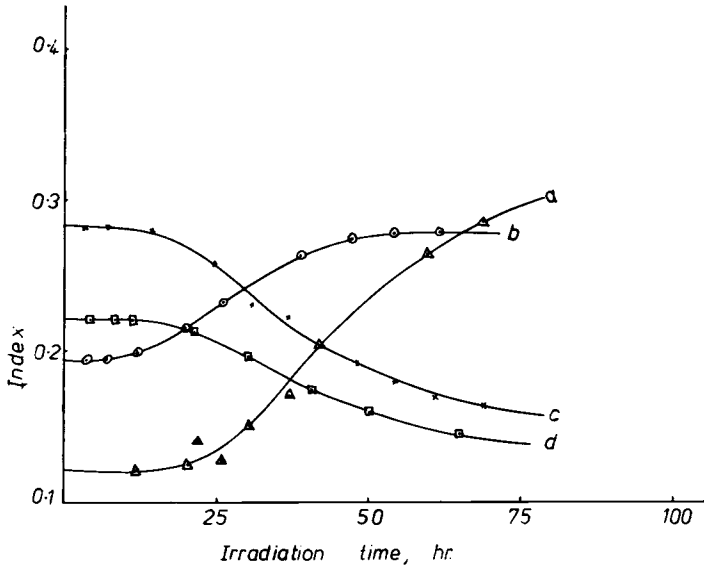


Fig. 2. Effect of EBHPT on functional group indices. Dependence of functional group indices on time upon UV irradiation. ABS + 1.0% EBHPT added as masterbatch (after extraction): (a) carbonyl index; (b) hydroxyl index; (c) carbon-carbon bond at 965 cm^{-1} ; (d) carbon-carbon bond at 912 cm^{-1} .

in Figure 3. The figure clearly shows the chemical changes taking place during photo-oxidation of modified ABS. Again, both double bonds at 965 and 912 cm^{-1} decreased after initially exhibiting an induction period. The hydroxyl group at $3500\text{--}3400\text{ cm}^{-1}$ and the carboxyl group at 1720 cm^{-1} also exhibit in-

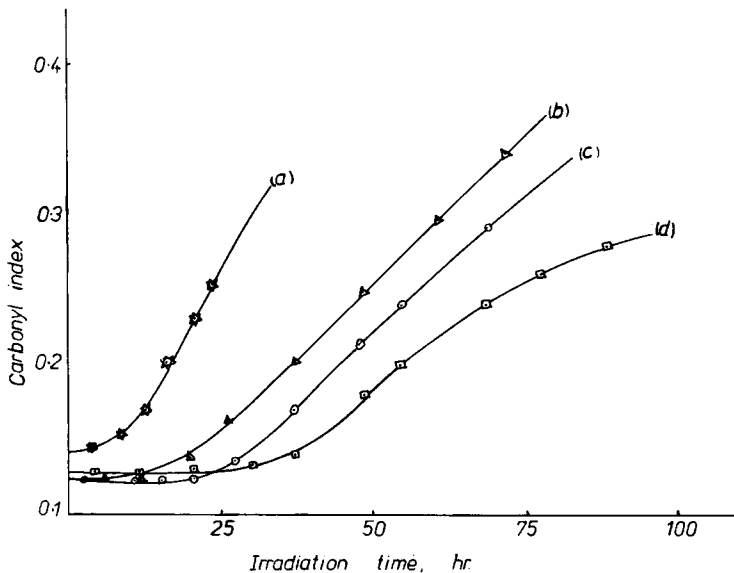


Fig. 3. Dependence of carbonyl index on UV irradiation time for ABS containing varying concentrations of EBHPT added as masterbatches (before extraction): (a) control—normal ABS; (b) ABS + 0.5% EBHPT; (c) ABS + 1.0% EBHPT; (d) ABS + 2.0% EBHPT.

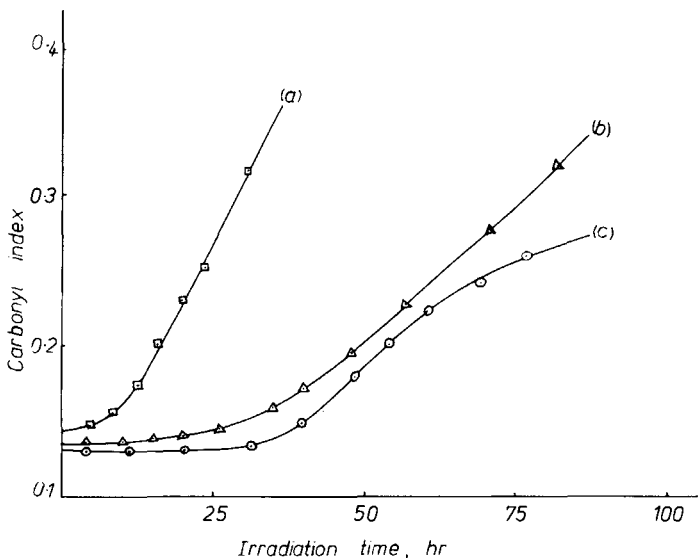


Fig. 4. Comparison of extracted and unextracted samples of ABS containing 2.0% EBHPT added as masterbatch: (a) normal ABS; (b) EBHPT 1.4 pph (extracted); (c) EBHPT 2.0 pph (unextracted).

duction periods. The end of the induction periods of the carbon-carbon double bonds corresponds to the end of the induction period in the hydroxyl group. The relative values of the indices seem to suggest that the point of attack by destructive agents is the double bond region in the polybutadiene backbone. This observation is in accord with the existing evidence.¹⁻⁴ The beginning of destruction of the double bonds also marks the start of the formation of the hydroxyl group which later rises to a plateau. This was found in all the cases studied. It is worth noting that even when the hydroxyl index has reached its maximum, the carbonyl index continues to rise.

Figures 3 and 4 show the dependence of the carbonyl index upon exposure time for various concentrations of ABS(M_2) (unextracted, Fig. 3; and extracted, Fig. 4). Figure 3 shows that the induction period is concentration dependent. Increased concentration of bound stabilizer (EBHPT) offers greater protection to the polymer. At about 2% bound EBHPT, it appears that autoretardation sets in. Table II shows the results obtained for induction periods and embrit-

TABLE II
Induction Periods (IP) and Embrittlement Times (ET) Produced by ABS(M_2) when Added to Normal ABS and Exposed to UV Irradiation^a

g Stabilizer/ 100 g ABS before extraction	g Stabilizer/ 100 g ABS after extraction	IP/ET before extraction, h	IP/ET after extraction, h
Control	—	3/24	3/24
2.0 (6.02×10^{-3})	1.40 (4.22×10^{-3})	32/90	25/70
1.0 (3.01×10^{-3})	0.70 (2.11×10^{-3})	20/71	17/65
0.5 (1.51×10^{-3})	0.35 (1.05×10^{-3})	11/52	9/48

^a Figures in parentheses are the molar concentrations of the added stabilizers per 100 g polymer.

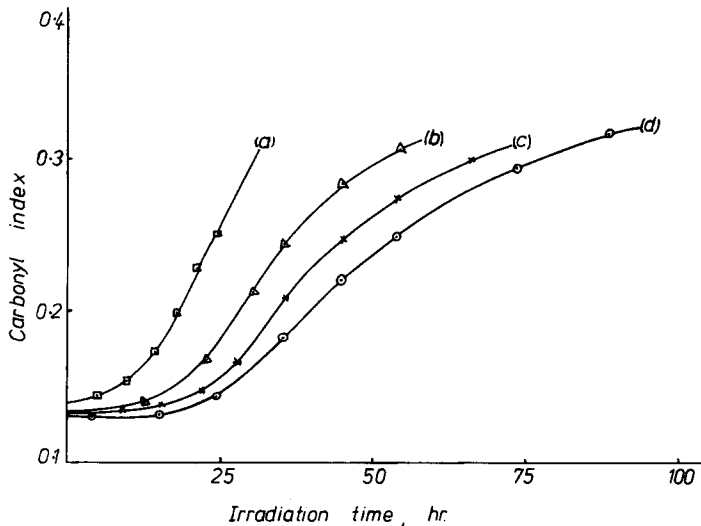


Fig. 5. Dependence of carbonyl index in ABS on UV irradiation time of ABS stabilized with UV 531 (unextracted): (a) normal ABS; (b) ABS + 0.5% UV 531; (c) ABS + 1.0% UV 531; (d) ABS + 2.0% UV 531.

tlement times for ABS films containing ABS(M₂) before and after extraction. Figure 4 shows that even after extraction the polymer remains highly protected from UV degradation by the bound stabilizer added as masterbatch. In other words, grafting of the UV stabilizer onto ABS makes the polymer resistive toward environmental degradation because the UV absorber cannot be extracted or leached.

Figure 5 shows the plot of carbonyl index as a function of exposure time for a commercial stabilizer UV 531. The stabilizer was added to ABS during processing operations. The figure has the same general features as Figures 3 and 4 for ABS containing EBHPT. The efficiency of UV 531 is shown in Table III.

Thermal Oxidative Degradation

It has been pointed out by many workers^{5,6} that the rubber segment in ABS is the chief point of attack by oxygen during processing operation, giving rise to allylic hydroperoxide which plays a major role in thermal oxidation of rubber-modified polymers. Part of the present study involves the incorporation of an

TABLE III
Induction Periods and Embrittlement Times Produced by UV 531 when Added to Normal ABS^a

g Stabilizer/100 g ABS	IP/ET before extraction, h	IP/ET after extraction, h
Control	3/24	3/24
2.0 (6.13×10^{-3})	15/57	9/34
1.0 (3.07×10^{-3})	11/45	5/28
0.5 (1.53×10^{-3})	7/29	4/24

^a Figures inside parentheses are the molar concentrations of the added stabilizers per 100 g polymer.

antioxidant, BHBM, a powerful hydroperoxide decomposer in the form of masterbatch ABS(M₁) to normal ABS to arrest the hydroperoxide which will otherwise be formed and lead to oxidation of ABS. Five concentrations of the masterbatch containing varying amounts of BHBM, [ABS(M₁)] were used. It was found from a measurement of torque against time that ABS(M₁) had the effect of increasing the ease of processing of ABS.

Both the unextracted and extracted samples were studied, and the results obtained are presented graphically in Figures 6 and 7. Figures 6 and 7 show the plot of carbonyl index as a function of heating time for the various concentrations of ABS(M₁) for unextracted and extracted samples, respectively. In both cases, the general shapes of the curves are similar. The unextracted samples exhibit longer induction periods than the extracted samples. The unstabilized polymer shows an induction period of 3 h, whereas the induction period of a 1% dilution is several times more. The induction period is also concentration dependent. At the end of the induction period, the oxidation rate proceeds quite fast. The extracted samples also display long induction periods compared with the unstabilized samples. On the average, the efficiency falls by about 14% after extraction. In all the concentrations studied, the embrittlement times were measured. Table IV displays the induction periods and embrittlement times obtained in these studies. Also Tables IV and V compare the performance of BHBM as an antioxidant and as a UV stabilizer, respectively. It could be seen that while BHBM is an excellent antioxidant, it is a very poor UV stabilizer.

Synergistic Mixtures

Perhaps the most interesting and the most technologically useful aspect of the work of this nature is finding suitable combinations of antioxidant ABS(M₁) and UV stabilizer ABS(M₂) which will give rise to synergism. In this work,

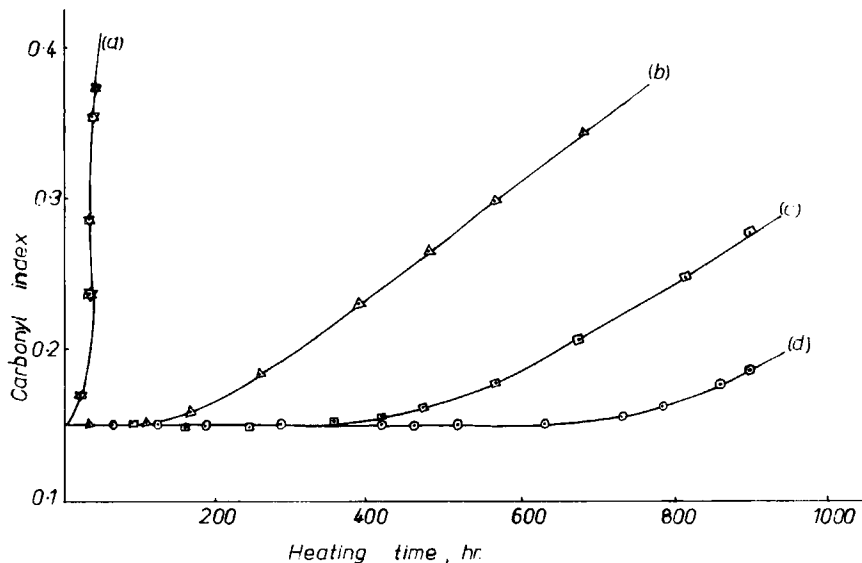


Fig. 6. Thermal oxidation of ABS at 100°C in air. Dependence of carbonyl index in ABS on heating time at various concentrations of BHBM added as masterbatches: (a) normal ABS; (b) 0.25% BHBM; (c) 0.5% BHBM; (d) 1.0% BHBM.

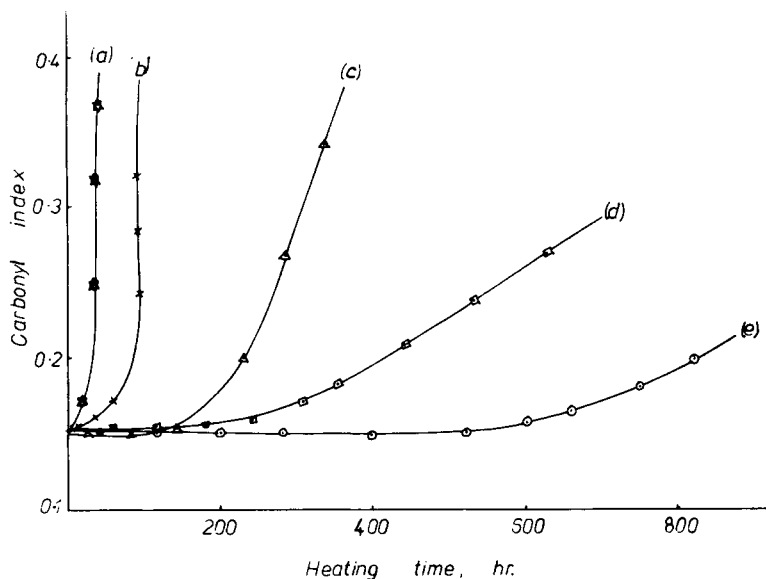


Fig. 7. Thermal oxidation of ABS in air at 100°C. Dependence of carbonyl index in ABS on heating time at various concentrations of BHBM added as masterbatch (after extraction): (a) normal ABS; (b) ABS + 0.08% BHBM; (c) ABS + 0.2% BHBM; (d) ABS + 0.4% BHBM; (e) ABS + 0.8% BHBM.

various ratios of the masterbatches have been mixed, and each case gave rise to synergism.

Figure 8 shows the dependence of carbonyl index upon irradiation time for two different ratios of ABS(M_1) and ABS(M_2) for extracted and unextracted samples. It is easy to see the effect of the bound antioxidant and UV stabilizer on the rate of oxidation of ABS. Under UV light, considerable protection is being

TABLE IV
Induction Periods and Embrittlement Times Produced by ABS(M_1) when Added to Normal ABS and Heated in Air Oven at 100°C

g Stabilizer/100 g ABS before/after extraction	IP/ET before extraction, h	IP/ET after extraction, h
Control	4/30	4/30
0.1/0.08	30/100	25/85
0.25/0.20	140/410	120/320
0.50/0.40	360/780	320/584
1.0/0.80	680/1500	600/1069

^a The above samples were also exposed to UV irradiation.

TABLE V

g Stabilizer before extraction	Induction period/embrittlement time, h
1.00	6/35
0.50	4/30
0.25	4/30
0.10	3/26

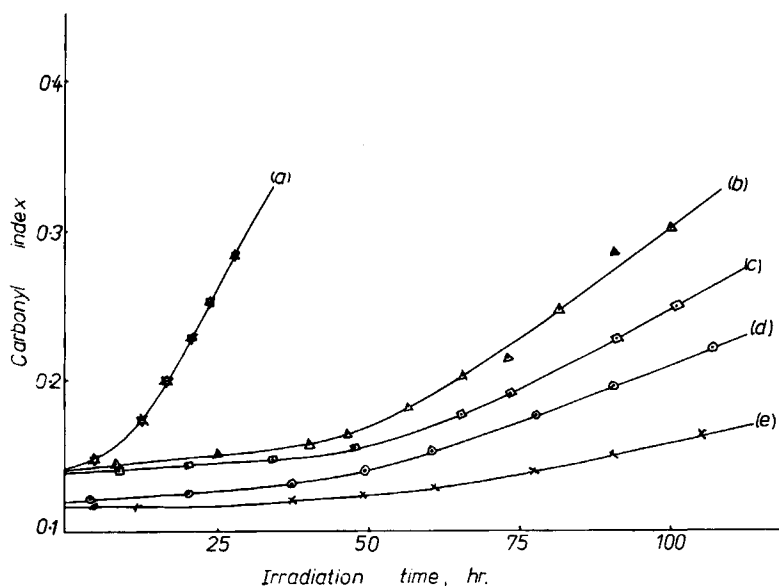


Fig. 8. Photo-oxidation of ABS containing synergistic mixtures of BHBM and EBHPT added as masterbatches: (a) normal ABS; (b) BHBM/EBHPT (1:2) extracted; (c) BHBM/EBHPT (1:1) extracted; (d) BHBM/EBHPT (1:1) unextracted; (e) BHBM/EBHPT (1:2) unextracted.

offered to the polymer. It can be seen in each case of various combinations studied that the performance of the protected polymer is by far superior to the individual masterbatches. The induction periods and embrittlement times were measured and are tabulated in Table VI. From this table, the superiority of the synergistic mixtures over the control cannot be overemphasized.

This is also demonstrated in Figure 9, where ABS containing a mixture of 1% BHBM in ABS(M_1) and 1% EBHPT in ABS(M_2) has been compared with ABS containing the same levels BHBM in ABS(M_1) and EBHPT in ABS(M_2) added individually. From this graph it can be seen that even after the end of the induction period for ABS containing synergistic mixtures of ABS(M_1) and ABS(M_2), the rate of change in slope is very small compared with other graphs. The slow rate of change in slope can be interpreted to mean higher degree of protection of the polymer by the additives. A low rate of oxidation suggests a

TABLE VI
Induction Periods and Embrittlement Times Produced by Mixtures of ABS(M_1) and ABS(M_2) when Added to Normal ABS and Exposed to UV Irradiation at about 30°C

g BHBM in ABS(M_1) per 100 g ABS unextracted/ extracted	g EBHPT in ABS(M_2) per 100 g ABS unextracted/ extracted	(BHBM)/(EBHPT) in 100 g ABS	IP/ET unextracted, h	IP/ET extracted, h
Control	—	—	3/24	3/24
1.0/0.8	1.0/0.7	1/1	65/186	55/160
1.5/1.2	1.0/0.7	1.5/1	50/150	40/138
2.0/1.6	1.0/0.7	2/1	40/150	38/138
1.0/0.8	2.0/1.4	1/2	75/220	65/186

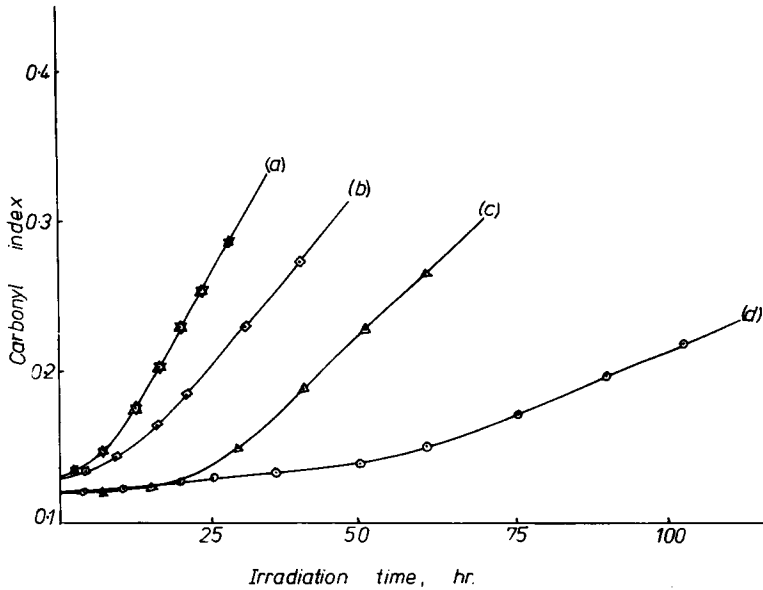


Fig. 9. Photo-oxidation of ABS. Dependence of carbonyl index in ABS upon UV irradiation time of unextracted ABS films containing BIBM and EBHPT and synergistic mixtures: (a) normal ABS; (b) ABS + 1.0% BIBM; (c) ABS + 1% EBHPT; (d) ABS + 1% BIBM + 1% EBHPT.

low rate of removal or destruction of the synergistic mixtures, and this is also reflected in Table VI. ABS containing the above mixtures was also studied in accelerated oven aging, and the results are presented graphically in Figure 10.

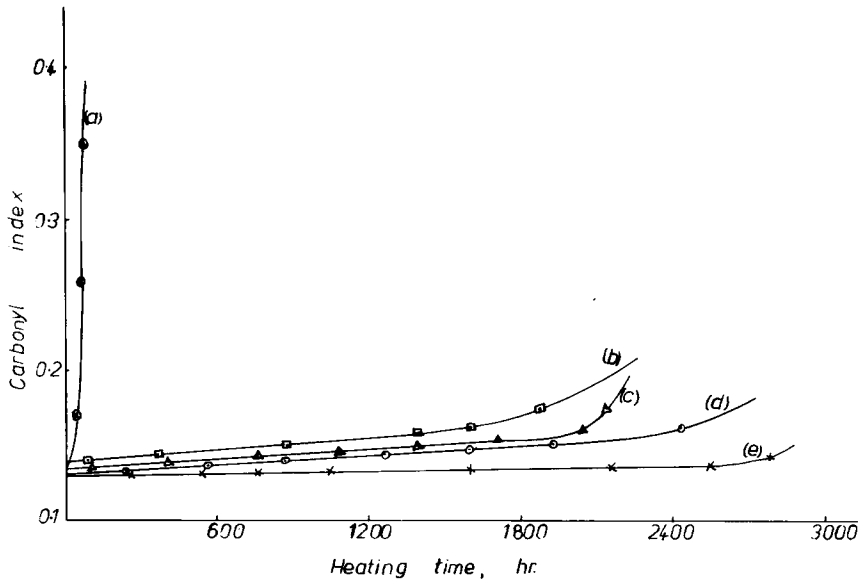


Fig. 10. Thermal oxidation of ABS containing varying ratios of BIBM/EBHPT at 100°C in air: (a) normal ABS; (b) EBHPT/BIBM (2:1); (c) EBHPT/BHDM (1:2); (d) EBHPT/BIBM (1:1); (e) EBHPT/BIBM (1:1.5).

It can be seen from the very long induction periods that the mixture offers considerable protection to the normal ABS when heated in air at 100°C.

CONCLUSIONS

The bound antioxidant and the UV stabilizer are concentrated in the rubber phase of the ABS polymer and cannot be readily extracted. The induction periods and embrittlement times were found to depend on the concentration of the added masterbatches reaching a maximum at 2% addition. In the case of the synergistic mixtures, the mixture containing 2% bound EBHPT in ABS(M₂) and 1% BHBM bound in ABS(M₁) gave the best performance under UV irradiation, where the mixture containing 1% EBHPT bound in ABS(M₂) and 1.5% BHBM bound in ABS(M₁) gave the best performance when heated in an air oven. The combination of UV absorber and antioxidant gives a very good stabilizer for ABS. The addition of these compounds in the form of masterbatches appears to be a practical way of incorporating them in ABS simply by dilution of ABS and gives thermal and stabilizing effects that cannot be achieved by stabilizers added in a conventional way.

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