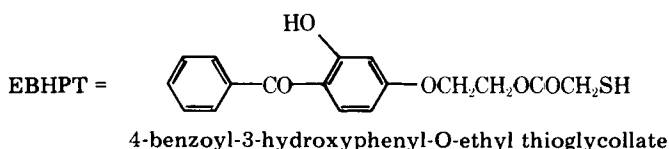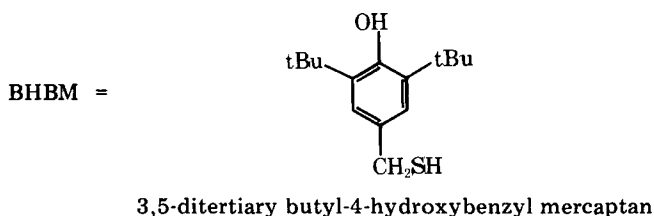# Environmental and Thermal Oxidation of Poly(vinyl Chloride) and Impact-Modified Poly(vinyl Chloride). I

INTRODUCTION

Some of the greatest deficiencies of PVC for many applications, particularly for building and sewage in the tropics, are its poor impact resistance, poor tensile strength, and discoloration when used outdoors. To improve these properties rubber-based polyblends are usually added to PVC. Unfortunately, the rubber phase is so easily degraded under UV irradiation and from being outdoors so much that its impact and tensile strengths, which largely account for its usefulness in engineering, is readily lost. It has been shown in a recent study that ABS acts as a suitable impact modifier for PVC.[1,2] But such impact-modified PVC have very poor stabilities, particularly in terms of photo and thermal oxidation.[1,2] However, in the present study, we have modified PVC by blending it with previously chemically modified ABS. Unlike the previous workers,[1,2] we have used mixtures of BHBM-rubber adduct, which is a powerful antioxidant (hereafter referred to as [ABS(M₁)] and EBHPT-rubber adduct [ABS(M₂)], which is a thio-based UV stabilizer, as modifiers/stabilizers for PVC. It has been shown in a previous study[3] that a synergistic mixture of both adducts (added as master batches) gave satisfactory protection for ABS during thermal and photooxidative degradation.

Note:

BHBM =

3,5-ditertiary butyl-4-hydroxybenzyl mercaptan

EBHPT =

4-benzoyl-3-hydroxyphenyl-O-ethyl thioglycollate

EXPERIMENTAL

Materials

Commercial PVC (solvic 223), ABS (having 30% PB, 45.5% S, and 22.2% AN) were used. Thermal stabilizer (tin maleate) and internal and external lubricants for PVC were added. ABS used was obtained by coagulating from the sample cycolac R211 supplied by Borg Warner.

Processing

Films of 2–2.5 × 10⁻³ in. thick were obtained by two methods:
(1) The polyblends were mixed in a RAPRA torque rheometer at 170°C for various lengths of time ranging from 3 to 10 min at 60 rpm⁻¹. Films were pressed at 190°C for 2 min. Thicker films were used for impact measurement.

0021-8995/80/0025-2133$01.00

(2) The polyblends were cast into films on a clean mercury surface from CH_2Cl_2. Any gel present was usually filtered off before using.

Outdoor Exposure

For outdoor exposure, samples were mounted between two very thin plywood sheets in which nine holes of appropriate dimensions were cut. The film samples were placed centrally over the holes on one sheet before placing the other on top. The system was clamped to hold the films in position on the plywood, and placed outside the Chemistry Department of the Ahmadu Bello University, Zaria, Nigeria; weathering was allowed to proceed. Degradation was followed by infrared, tensile-strength, and impact-strength measurements, and the time to embrittlement was recorded.

Instrumentation

Infrared spectroscopy study was carried out on a Perkin–Elmer spectrophotometer model 700. Thermal oxidation was carried out in a Wallace air oven at a temperature of 100°C. The tensile strengths of the polyblend films were compared using the Instron testing machine model TM-M at a crosshead speed of 0.51 cm/min at room temperature of 25°C. The energy to break each film was measured at intervals during outdoor exposure.

RESULTS AND DISCUSSION

For all polyblends, the chemical changes which occurred had been followed by evaluation of the IR spectra. Figure 1 shows a typical spectra of processed polyblend exposed outdoor for various lengths of time. In all cases, the regions of greatest interest are the areas relating to the ketonic band at 1720–1725 cm^{-1} and the broad hydroxyl band at 3500–3400 cm^{-1}. Figure 2 shows the various plots of the carbonyl index as a function of time. The indices were expressed as the ratio of the absorbance of the growing or decaying peaks to that of the reference peaks. Also, in calculating the indices' corrections for slight variations in thickness, other experimental artifacts have been taken into consideration. The peak at 2910 cm^{-1} was used as the reference peak.

In Figure 2, curves 1, 2, and 5 show the effect of outdoor weathering on unstabilized ABS, PVC–ABS blend, and unstabilized PVC, respectively. The unmodified PVC has better resistance to outdoor weathering than ABS. Also, the presence of PVC in the PVC–ABS blend helps to improve the weatherability of ABS. Curves 4 and 7 in Figure 2 compare the effect of tin maleate stabilizer, Irgastab T_{290}, with ABS (M_1) when added as antioxidant for rigid PVC; while curves 3 and 6 compare the effect of a mixture of BHBM-rubber adduct and EBHPT-rubber adduct with a mixture of tin maleate stabilizer and ABS(M_2) on rigid PVC. The sample containing a mixture of ABS (M_1) and ABS (M_2) auto-oxidizes after an initial induction period as seen in Figure 2, curve 3.

In all cases, the general behavior of the films are quite similar. In all the samples of the blend, particularly those without tin maleate stabilizers, there appears to be two stages of degradation, i.e., an initial fast stage of degradation followed by a slow stage (curves 2, 3, 5, and 6). It has been suggested that the rubber component of ABS is highly susceptible to photooxidation, which usually
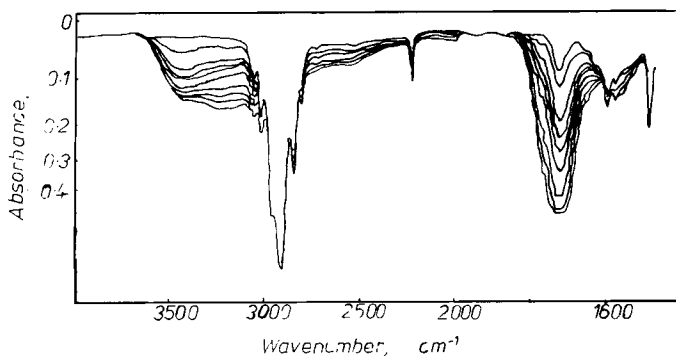

Fig. 1. Dependence of IR spectra on natural weathering of PVC–ABS blend. The blend contains 14.43% ABS. This sample has been exposed for 400 hr.
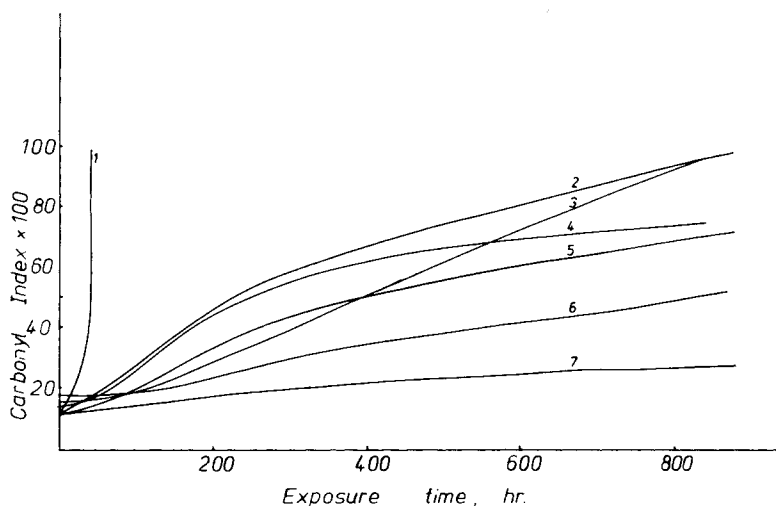
Fig. 2. Natural weathering of processed films in the presence of various additives. The ordinate shows the carbonyl index (A_{1725}/A_{2910}), while the abscissa indicates the exposure time in hours. Composition of various blends: (1) Unstabilized ABS; (2) ABS–PVC (ABS = 14.43%); (3) ABS(M_1) = 14.43%, ABS(M_2) = 14.43%, wax E = 0.63%, castearate = 0.76%; (4) ABS(M_1) = 14.43%, wax E = 0.63, castearate 0.76%; (5) PVC only; (6) ABS(M_2) = 14.43%, Irgastab T_{290} 2.4%, wax E = 0.63%, castearate = 0.63%, castearate = 0.76%.

leads to crosslinking of the phase accompanied by scission of the graft between the rubber and the matrix.[1] Also in the study of the individual components it has been observed that ABS photooxidizes faster than PVC.[3] Therefore, from Figure 2, it may be concluded that the first stage of oxidation (which is fast) is due to ABS and the second stage (which is slow) is due to PVC. A comparison of the stabilizing effects of tin maleate with ABS (M_1) and ABS (M_2) on PVC and impact-modified PVC shows that the tin maleate gives a better protection to PVC on outdoor exposure than ABS (M_1) or ABS (M_2) (curves 3, 6, and 7). However, it must be said that the presence of BHBM-rubber adduct and EBHPT-rubber adduct in the impact-modified PVC slows down the rate of weathering as evidenced from the values of the induction periods in Table I.

Thermal Oxidation of Processed Films of Impact-Modified PVC

It has been pointed out that the rubber segment in ABS is the chief point of attack by oxygen during processing operations while the loss of HCl initiates the degradation of PVC.[1,4] In the present study, BHBM-rubber adduct has been added to PVC to serve as an antioxidant just as it did in ABS.[3] The combination of ABS(M_1) and ABS(M_2) which gave a synergistic effect in ABS[3] has been added as stabilizer–modifier for rigid PVC and processed for various lengths of time. The results obtained on thermal oxidation have been presented in Figure 2 (curves 1–7) and in Table II.

TABLE I
Induction Periods Produced by Tin Maleate, ABS (M_1), and ABS (M_2)

Materials	AO[a]–stabilizer	Induction periods, hr
ABS	—	—
PVC	—	—
PVC–ABS	Tin maleate	260
PVC–ABS	ABS(M_1)	80
PVC–ABS	Tin maleate–ABS(M_2)	130
PVC–ABS	ABS(M_1)–ABS(M_2)	100

[a] AO = antioxidant. Above samples were also studied in oven ageing.

TABLE II
Thermal Oxidation of Impact-Modified PVC in the Presence of Tin Maleate, ABS (M_1), and ABS (M_2)

Materials	AO–stabilizer	Processing time, (min)	Induction period, hr
ABS	—	3	—
PVC	—	3	—
PVC–ABS	Tin maleate	3	800
PVC–ABS	ABS(M_1)	3	8
PVC–ABS	Tin maleate/ABS(M_2)	3	300
PVC–ABS	ABS(M_1)–ABS(M_2)	3	120
PVC–ABS	ABS(M_1)/ABS(M_2)	5	80
PVC–ABS	ABS(M_1)/ABS(M_2)	$7\frac{1}{2}$	40
PVC–ABS	ABS(M_1)/ABS(M_2)	10	10

Figure 3, curves (1, 2, and 5), show that of the three samples PVC was the most stable, while ABS was the least stable. Again, the PVC–ABS blend takes an intermediate position between pure ABS and pure PVC. Curves 3 and 7 compare the effect of BHBM-rubber adduct with tin maleate stabilizer. It is clear that the presence of ABS in the blend causes an immediate autooxidation in that the PVC–ABS blends show no induction periods. However, the presence of tin maleate stabilizer in PVC (curve 7) greatly resists thermal oxidation. Thus, it can be said that the presence of the rubber phase in the blend has done considerable damage to the blend (Table II).

Figure 3 (curves 4 and 6) shows that systems containing a mixture of tin maleate and ABS(M_2) give a more satisfactory protection to impact-modified PVC during thermal oxidation than does the system containing a mixture of ABS(M_1) and ABS(M_2). It can also be seen that after the induction periods, the rates of oxidation of these systems (as evidenced from the slopes of the curves 4 and 6) are greatly retarded when compared with the rates of oxidation of the systems reflected in curves 2 and 3. Table II also shows that long processing times do a lot of damage to the polyblends.

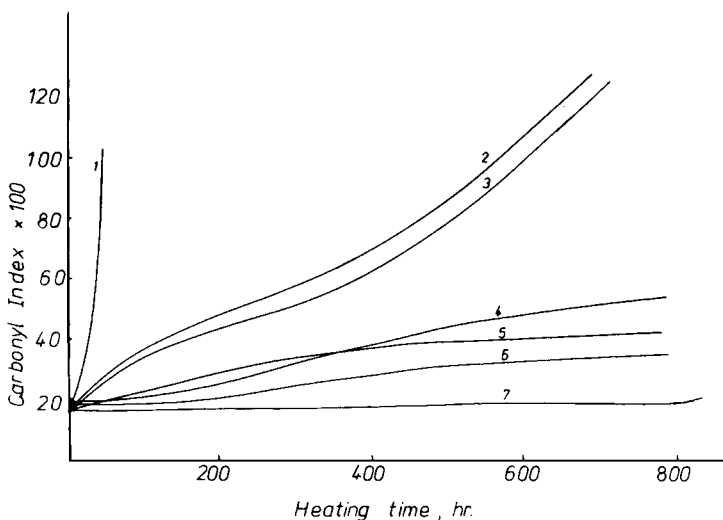Figure 4 shows the energy change corresponding to the time of outdoor exposure. The figure re-

Fig. 3. Thermal oxidation of processed films. Dependence of carbonyl index (A_{1725}/A_{2910}) upon heating time in air at 100°C. Composition of blends: (1) Unstabilized ABS; (2) ABS–PVC (ABS = 14.43%); (3) ABS(M_1) = 14.43% wax E = 0.63%, castearate = 0.76%; (4) ABS(M_1) = 14.43%, ABS(M_2) = 14.43%, wax E = 0.63%, castearate = 0.76%; (5) PVC only; (6) ABS(M_2) = 14.43% Irgastab T_{290} = 2.4%, castearate = 0.76%, wax E = 0.63%; (7) Irgastab T_{290} = 2.4%, wax E = 0.63%, castearate = 0.76%.
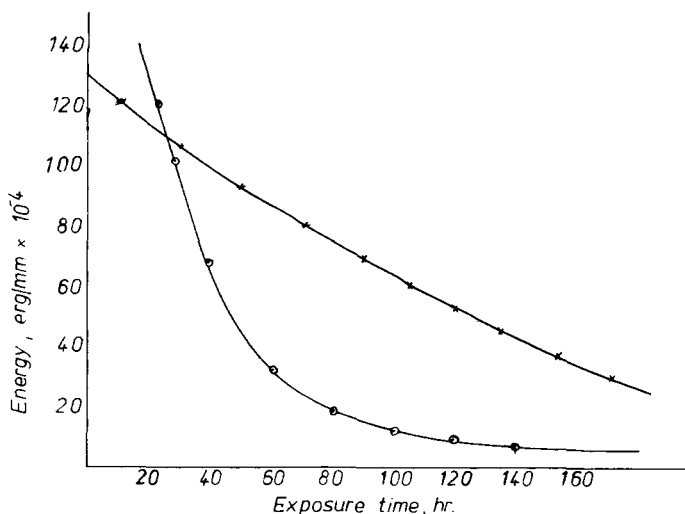
Fig. 4. Effect of outdoor exposure on the falling-weight impact resistance of PVC and impact-modified PVC. (x), processed PVC, (⊙), impact-modified PVC.

veals that the impact resistance is very much higher initially for PVC containing BHBM-rubber adduct than for rigid PVC. However, the impact-modified PVC degraded very rapidly after about 30 hr exposure. It actually falls below that of PVC.

Cast films

Figure 5 shows typical stress–strain relationships for various PVC–ABS ratios. This figure reveals that as the amount of ABS in the blend increases, the elastic region decreases. The curves show a gradual transition from elasticity to plasticity. Curves a, b, and c in Figure 6 show the plots of elongation at break, ultimate tensile strength, and Young's modulus against composition, respectively. As the amount of ABS in the blend decreases, the elongation increases. With increase in the amount of PVC in the blend, both the tensile strength and the modulus increase, i.e., the structure becomes more and more rigid.

SUMMARY

Acrylonitrile butadiene styrene (ABS), which has been previously stabilized against degradation by heat (using thio-based BHBM-rubber adduct) and UV irradiation (using thio-based EBHPT-rubber adduct), has been added in the form of master batches to modify PVC. It was found that
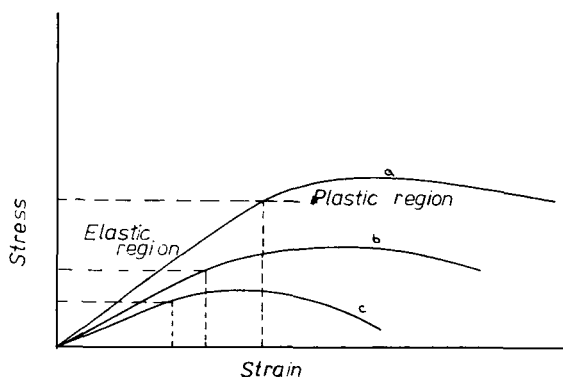

Fig. 5. Graphical representation of stress–strain curve produced by the blends. (a), PVC; (b), PVC–ABS blend; (c), ABS.
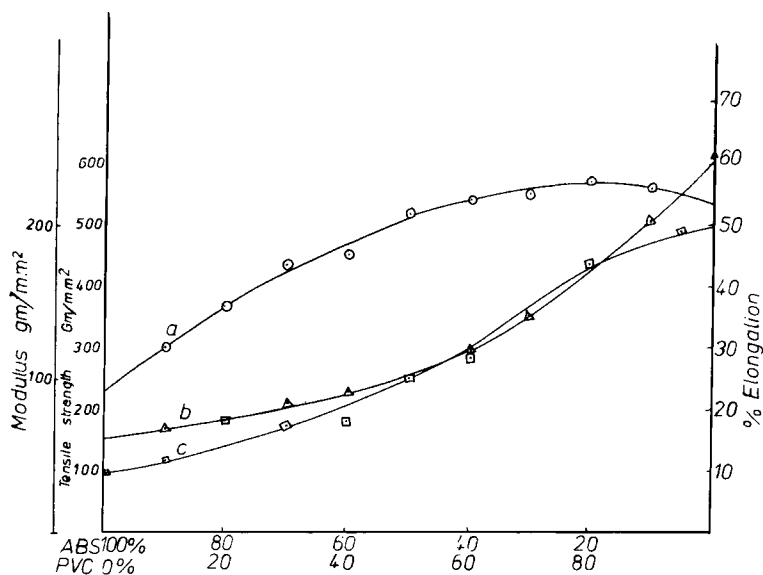
Fig. 6. Graph of (a) elongation at break, (b) ultimate tensile strength, and (c) Young's modulus against composition.

previously stabilized ABS gave no protection to PVC—the weatherability was grossly reduced chemically and physically. However, a combination of commercial stabilizer Irgastab T_{290} and a thio-based UV stabilizer (added as a master batch) gave relatively good protection to PVC against thermal aging and outdoor exposure. The commercial thermal stabilizer proved better than the thio-based thermal stabilizer (added as master batch) for stabilizing impact-modified PVC. The investigations carried out on cast blends show that as the percentage of PVC in the blend increases, the structure becomes more rigid.

References

1 G. Scott, International Conference on Toughening of Plastics, 1978.
2. G. Scott, and M. Tahan, *Eur. Polym. J.*, **13**, 989 (1977). (b) **13**, (1977).
3. E. G. Kolawole, unpublished results.
4. G. Scott, in *Atmospheric Oxidation and Anti Oxidants,* Elsevier, London, 1965.

E. G. KOLAWOLE
G. E. MBAMALI
J. Y. OLAYEMI

Department of Chemistry
Ahmadu Bello University
Zaria, Nigeria