

Environmental Degradation of Some Polymer Blends. Blends of Polystyrene with Acrylonitrile Butadiene Styrene, Poly(vinyl Chloride), and Polybutadiene and Blends of Polybutadiene with Poly(vinyl Chloride)

E. G. KOLAWOLE and M. O. AGBOOLA, *Department of Chemistry,
Ahmadu Bello University, Zaria, Nigeria*

Synopsis

One class of polymer/additive which has become increasingly important is polymer blends. In this study the ultimate tensile strength, elongation at break, and the modulus of acrylonitrile-butadiene-styrene, poly(vinyl chloride), polybutadiene and polystyrene and their blends have been studied over an entire binary composition range. We have correlated these mechanical properties to their degradation behavior under natural and accelerated weathering by measurement of various indices during thermal and natural weathering. It was found that during natural weathering the presence of polystyrene in acrylonitrile-butadiene-styrene (ABS) improved the weatherability of ABS; the converse was true when the blends were heated in an air oven at 100°C. It was also found that the weatherability of PB was improved in the presence of polystyrene and large improvement in the rigidity was observed. Similarly, from a measurement of carbonyl index, it was found that PVC has a stabilizing effect on PB. In many cases, the 50:50 composition of the polymers gave the best compromise of good mechanical properties, heat stability, and outdoor weathering. The mechanisms of possible interactions between the degrading polymers are discussed.

INTRODUCTION

There is no doubt that studies on polymer blends or mixtures of polymers are now the subject of considerable commercial interest. It is well established that under degradation conditions considerable interactions may occur between the constituents of the blends, leading to quite new degradation reactions which may have effects on the subsequent applications of the materials. Over the past 10 years a systematic study of some polymer blends had been carried out in various laboratories in the world.¹ Some of these workers² concentrated their attention on high temperature degradation of the blends with a view to finding out the products of such degradations. Pairs of polymers studied include blends of polystyrene with polypropylene,³ polyacrylate,⁴ poly(methylmethacrylate),⁵ blends of polypropylene with poly(methylmethacrylate),^{6,3} poly(vinyl acetate) with poly(methylmethacrylate),⁷⁻⁹ poly(vinyl chloride) with poly(methylmethacrylate).¹⁰ Paul^{11,12} and his co-workers have studied the mechanical properties of ternary mixtures of polymers. All these workers were not concerned with the ultimate stability of these blends. They did not pay attention to what happens to the blend under degradative conditions such as irradiation by UV light, oxidative degradation in the presence of oxygen, and other degradative agents.

Of the commonly used polymers in the developing polymer industry in Nigeria,

polyethylene, polystyrene, poly(methylmethacrylate), and poly(vinyl chloride) have become very important. The use of polymer blends to improve some of the desired properties of the homogeneous polymers is yet to gain ground in this country. In the present study, we have blended some of these polymers together with ABS terpolymer in an attempt to modify their mechanical properties. We want to know how the stabilities of the polymers and those of their blends are affected by some degradative agencies in tropical weather. UV irradiation from sunlight is an important factor in polymer degradation, and we took particular interest in assessing the effect of radiation to which a polymer film has been exposed during its life history. We have also tried to relate the mechanical properties to the aging of the blends. We have also studied the effect of prolonged heating in the life of a polymer blend and how it affects the mechanical properties. In the present work, we present the results obtained for the blends of poly(vinyl chloride) (PVC) with polybutadiene (PB), and the blends of polystyrene (PS) with acrylonitrile-butadiene-styrene (ABS), poly(vinyl chloride) and polybutadiene. Subsequent references to these materials will employ these abbreviations.

EXPERIMENTAL

Materials

Polystyrene crystals were supplied by RAPRA, acrylonitrile butadiene styrene was supplied by Borg-Warner in latex form as Cylcolac R211, polybutadiene was supplied by Dunlop (Nig.) Ltd., and poly(vinyl chloride) (solvic 223) was supplied by Allied Chemicals (Nig.) Ltd. All these samples contain no additives. Some of them were reprecipitated from appropriate solvents for improved purity.

Sample Preparation

Films were cast from a solution containing both polymers on to a clean mercury surface in a desiccator. The following solvents were used for the following blends: PS/ABS—chloroform; PS/PB—toluene; PS/PVC—chlorobenzene; and PB/PVC—toluene. An atmosphere of nitrogen under reduced pressure was maintained for 48 h. The films were finally dried to constant weight *in vacuo* at room temperature. Blends of various compositions were cast in this way.

General Weathering Procedure

Outdoor Exposure

The outdoor weathering of the films was carried out by exposing the films outside the Chemistry Department of Ahmadu Bello University, Zaria, Nigeria. Sample films were mounted between two very thin plywoods in which holes of appropriate dimensions were cut out. 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 and weathering was allowed to proceed. Films of even thickness of 0.020 cm were used for the (carbonyl, hydroxyl, carbon-carbon unsaturation) measurements. For the mechanical properties film samples of 5.0 × 0.70 × 0.020 cm were similarly mounted over the slits on already

prepared plywoods and similarly exposed. Measurements were carried out on each sample before exposure and at intervals during the exposure.

Heating Procedure

Accelerated thermal oxidation of the films were carried out by mounting the sample films on specially prepared cardboard holders and were suspended with copper wires in the cavity of the Wallace air oven at 100°C. Each sample film was contained in a separate cavity. Degradation was then followed by running the IR of the films before heating and at intervals during heating.

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 towards the person holding the film, and the second was carried out by bending away from the person holding the film. This was a severe test for the polymer films.

Instrumentation

Infrared absorption spectra were recorded using a Perkin-Elmer IR Spectrophotometer Model 1000. For quantitative purposes, all spectra were scanned on transmission paper rather than on a logarithmic scale. This was done in order to minimize any intensity loss due to reflection at the outer and inner sample surfaces.¹³ The evaluation of degradation due to outdoor exposure or thermal exposure by IR methods was done by following the increase in carbonyl absorption peaks appearing around 1720 cm⁻¹ and the hydroxyl peaks appearing around 3450 cm⁻¹ in all blends. In each of the polyblends, a peak characteristic of one of the polymers itself was used as a reference peak, e.g., for PS/ABS polyblends, the peak appearing at 2220 cm⁻¹ was used as a reference. The results were expressed as carbonyl index or hydroxyl index as the case may be; e.g., for PS/ABS,

$$\text{carbonyl index} = A_{1720}/A_{2220} \text{ for differing exposure/heating times}$$

$$\text{hydroxyl index} = A_{3450}/A_{2220} \text{ for differing exposure/heating times}$$

The mechanical properties of the films were compared using the Instron Testing Machine Model TM-M at a crosshead speed of 10.0 cm/min at a room temp of 25°C.

RESULTS AND DISCUSSION

Blends of polystyrene (PS) and acrylonitrile-butadiene-styrene (ABS).

The stability of PS/ABS blends towards environmental degradation has been studied. In this study, mechanical as well as chemical properties of the blends have been measured as a function of time of outdoor exposure and heating.

Outdoor Exposure

A series of experiments were carried out with PS/ABS blends of composition ratios from 10:0 to 0:10 by weight in order to investigate the behavior of the mechanical properties of degraded and undegraded samples. The result obtained from the mechanical and chemical studies of the various compositions of PS and ABS have been presented graphically in Figures 1-5.

In the mechanical properties studied, attention has been focussed on the stress-strain relationships, elongation at break, ultimate tensile strength, and the modulus of the blends. Figure 1 shows the stress vs. strain curves for the various ratios of PS:ABS in the blends. It can be seen that PS behaves as a typical hard and brittle polymer while ABS behaves characteristically as a soft and tough polymer. The progressively decreasing area under the curve (at break point) as the amount of ABS in the blend decreases indicates a decrease in the impact strength of the blend.

Figure 2 shows a summary of the mechanical properties of the blends. It can be seen from Figure 2 that elongation decreases with increase in the amount of PS in the blend; so does tensile strength but in each case passing through a minimum. In other words, the strengths and elongations of the blends are less than those of the pure components. This means that in terms of these two properties, the blends are probably less superior to the homopolymers. The modulus, on the other hand, falls very rapidly between 0% and 25% PS in the blend and thereafter exhibits a gentle fall. Each of properties represented in Figure 2 had been carefully investigated for the blends. We noticed that the films became thickened and hard on exposure for a fairly long time. The elongation at break decreased with increase in time of exposure or heating. The percentage elongation was also found to vary with the composition of the blend,

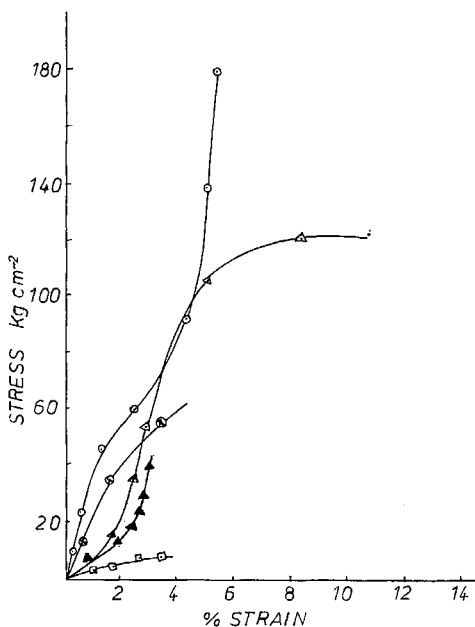


Fig. 1. Graphical representation of stress-strain curves produced by the blends: (○) 100% PS; (△) 100% ABS; (⊙) 50% ABS/50% PS; (▲) 75% ABS/25% PS; (□) 10% ABS/90% PS.

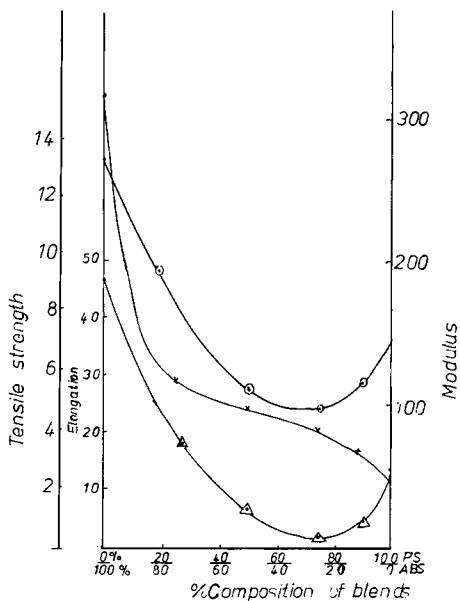


Fig. 2. Graph of dependence of mechanical properties on % composition of the blends: (O) Tensile strength; (X) modulus; (Δ) % elongation at break.

with a minimum occurring at 25% ABS in the blend. We also found that the ultimate tensile strength passes through a maximum with increase in time of exposure. The time to reach this maximum is composition-dependent. (The values plotted for ultimate tensile strength in Figure 2 are for one particular time.) The time to reach the maximum tensile strength was nearly equal to their embrittlement times. Beyond the maximum, the graph falls off. It was also found that, for each blend, the modulus increased with increase in time of outdoor exposure or heating. So to sum up, we find that both ultimate tensile strength and modulus increase with exposure or heating times whereas the elongation decreases. This phenomenon has been attributed to the degradation of PB backbone in ABS. ABS is very vulnerable to degradation by UV radiation or oxygen attack. It is the presence of polybutadiene that makes it difficult to improve its resistance towards photooxidation. Alkyl radicals and alkyl peroxy

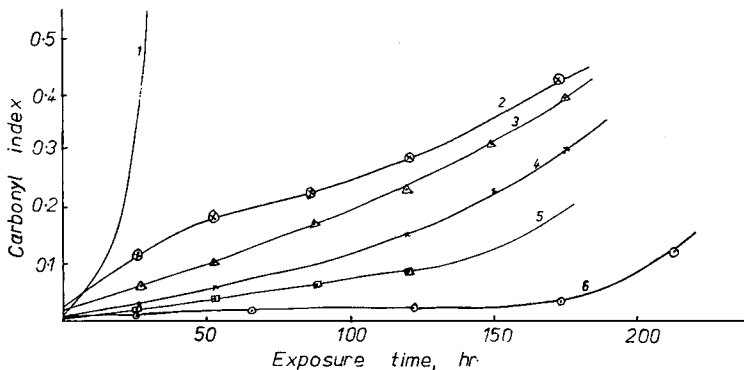


Fig. 3. Natural weathering of PS/ABS blends. Dependence of carbonyl index upon outdoor exposure time: (1) 100% ABS; (2) 75% ABS/25% PS, (3) 50% ABS/50% PS; (4) 25% ABS; 75% PS (5) 10% ABS/90% PS; 6-100% PS.

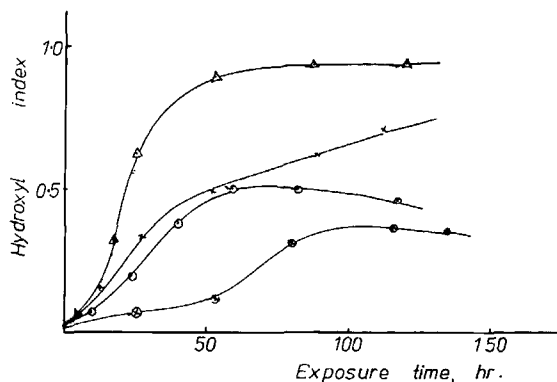


Fig. 4. Natural weathering of the PS/ABS blends. The ordinate shows the hydroxyl index while the abscissa indicates the exposure time in hours. (Δ) 100% ABS; (\times) 75% ABS/25% PS; (\circ) 50% ABS/50% PS; (\otimes) 25% OS.

radicals can readily form in ABS and polystyrene so that when both are degraded in the environment of one another, crosslinking is enhanced and greater rigidity will be observed. Thus the observed increase in tensile strength until a maximum is reached will probably correspond to the time when crosslinks are being built up. This also explains the observed increase in modulus with increase in exposure time. The sum total of these observations is that the presence of ABS in PS/ABS blends causes rapid degradation of the blends but at the same time makes the blend more rigid up to a certain point. It, however, leaves the blends less ductile.

Apart from the studies made on mechanical properties of the blends, the changes occurring in the microstructure were also studied using infrared spectroscopy. During the outdoor weathering and oven aging of the blends, developments of the carbonyl group at 1720 cm^{-1} , the hydroxyl group at 3450 cm^{-1} , the polytrans 1,4-butadiene at 965 cm^{-1} have been followed. The stability of the polyblends have been represented in Figure 3 where the carbonyl index has been plotted as a function of time. The work being reported here was carried

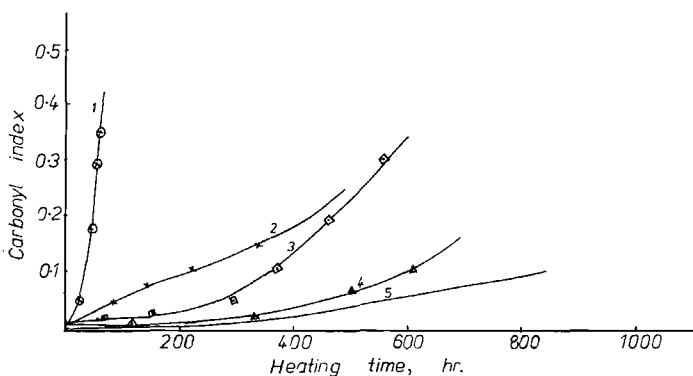


Fig. 5. Thermal oxidation of PS/ABS blends. Dependence of carbonyl index upon heating time in air at 100°C . (1) 100% ABS; (2) 10% ABS/90% PS; (2) 50% ABS/50% PS; (4) 75% ABS/25% PS; (5) 100% PS.

out between July 1978 and June 1980. During this period, the polymer samples have experienced the aggressively varying weather conditions of this country. The figures presented here represent typical results obtained from the various samples studied when exposed outdoors. In general, the pattern of variation were the same throughout the years.

For the degradation of PS two characteristic absorption bands at 3450 cm^{-1} and at 1720 cm^{-1} were followed. There were no marked increases in the absorption peaks with exposure time. This was also found to be true when PS was degraded in air oven at 100°C . This should not be too surprising because, although the mechanism of oxidation of PS has been a subject of much investigation and speculations, the question of initiation processes have not been settled once and for all. The importance of sample prehistory, the copolymerization of oxygen, and the significance of singlet oxygen are topics which are very relevant to the thorough elucidation of the initiation mechanism. Generally, it was found that PS was always brittle before showing any significant changes in the peaks. This might indicate low concentration of phenyl alkyl ketone end groups usually present in commercial sample. These groups are believed¹⁴ to be formed by the scavenging of residual oxygen in the polymerization processes to form polystyrene-oxygen copolymer. In this study, the embrittlement times obtained depended upon the time of the year—the harmattan period being the worst when polymer films used to crack before showing any growth in the relevant peaks. From Figure 3, it can be seen that PS alone appears to be the most stable of the blends, having an induction period of 155 h where other blends have no induction periods. The rate of degradation is greatest for pure ABS. We also see that the change in carbonyl concentration increases with increase in the amount of ABS in the blends. In each case the curve rises to a peak and falls off. Similar observations have been made in our earlier studies.^{15,16} This observation has been carefully explained in those publications.

The above polymer samples have been heated in the Wallace air oven. Figure 5 shows the dependence of the carbonyl index on heating times. Under thermal oxidation ABS degraded fastest and PS was the least degraded. Again it can be seen at a glance that, under thermal oxidation, PS has a stabilizing effect on ABS by the introduction of induction periods. From the study of the homopolymers, the degradation of ABS would begin before that of PS. From Figure 5, it would appear that during the period when ABS is breaking down, the PS degradation is halted. When ABS is breaking down, some of the products of degradation (from PB backbone) may diffuse into the PS phase (since both are in each other's environment), which then could act as radical inhibitors by losing an H atom to the polystyrene radical with the formation of allylic type radicals which are of relatively low reactivity—thus PS may be stabilized in the presence of ABS. Another way of looking at it is that ABS may have a sensitizing effect on pure polystyrene. It is very interesting to know that the blend containing 75% ABS and 25% PS shows the greatest thermal stability for the blends whereas the reverse is the case under natural weathering. Thus, for articles requiring ABS in thermal operations, PS could be added to cheapen the cost and also obtain improved performance. This technique will also find application in coextrusion to solve the important economic problems of scrap recycling.

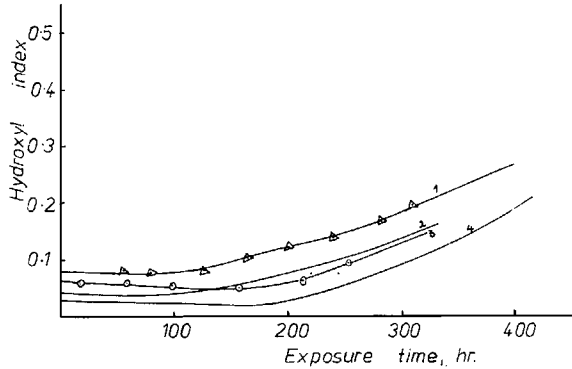


Fig. 6. Natural weathering of PS/PVC blends. The ordinate shows the hydroxyl index while the abscissa shows the time of outdoor exposure. (1) 100% PVC; (2) 100% PS; (3) 75% PVC/25% PS; (4) 50% PVC/50% PS.

Blends of Polystyrene and Poly(vinyl Chloride)

In this study we have used polystyrene (PS) crystals which contain no additives. Our attention has been focussed on the changes occurring in the physical properties as well as changes in the microstructure of the films when exposed outdoors in our environment and also when heated in the Wallace air oven. The films were cast from chlorobenzene containing both polymers at different desired ratios.

For changes occurring to the microstructure, IR spectra of the films were recorded before outdoor exposure or thermal oxidation and at regular intervals. The carbonyl development at 1720 cm^{-1} and the hydroxyl development at 3450 cm^{-1} have been followed. Figure 6 shows the dependence of the hydroxyl index upon exposure time. In terms of hydroxyl development, all blends show considerable stability under outdoor weathering when compared with the pure polymers. The calculated values for OH index were less for the polyblends than for the pure polymers. This means that both polymers exhibit cooperative stabilizing effects on each other.

Figure 7 shows the carbonyl index dependence on exposure time. In terms of carbonyl development, it is seen that at any time an increase is observed in the case of PVC, whereas PS shows no drastic increase until it embrittled. The polyblends take intermediate positions. This observation has been interpreted

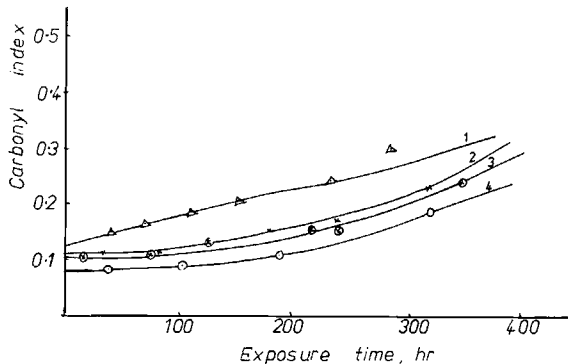
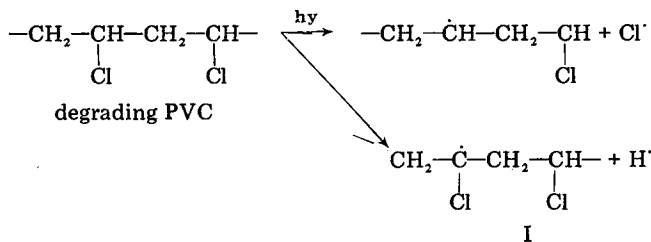
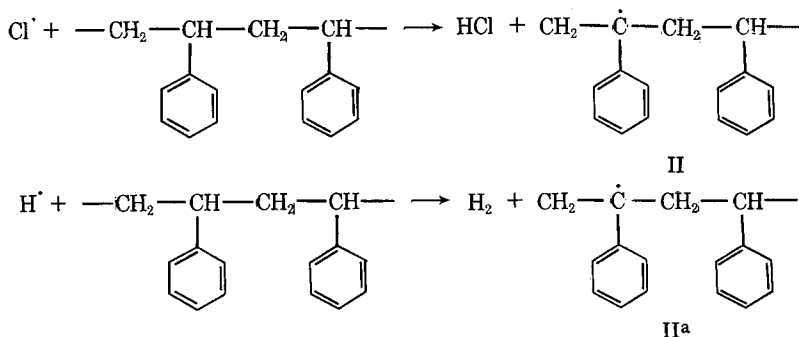


Fig. 7. Natural weathering of PS/PVC blends. Dependence of carbonyl index on exposure time. (1) 100% PVC; (2) 50% PVC/50% PS; (3) 75% PVC/25% PS; (4) 100% PS.

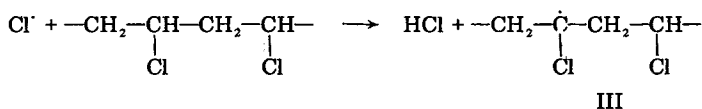
in terms of their stabilities towards environmental degradation. The polyblends show great stability towards environmental degradation with the 1:1 PVC/PS blend having an induction period of 220 h and the 3:1 PVC/PS having an induction period of 175 h. The stability of the blends on exposure outdoors cannot, however, be fully explained by their average composition. Similar observations have been made for the polyblends heated in an air oven at 100°C. Generally, we find that the degradation of PVC is delayed in the presence of PS. It is suggested that there is some interaction between the degrading polymers. The observed stabilizing effect of the PS on the PVC might be explained as follows:



The chlorine radical from the degrading PVC can abstract hydrogen atoms from polystyrene, producing polystyryl radicals. Similarly the hydrogen radical can abstract hydrogen from PS, again producing polystyryl radicals and hydrogen gas:



The tertiary hydrogen atom in PS is more readily abstracted than that on PVC (III) by chlorine radical because of the presence of the benzene ring, which is electron-releasing while chlorine attached to the tertiary carbon in PVC is electron-withdrawing. A more important reason for the preferential abstraction of the tertiary hydrogen on the PS by the chlorine or hydrogen radical is the fact that the radical so produced is more stable than that produced by a similar attached on the PVC. The stability of the polystyryl radical is due mainly to the resonance stability caused by the presence of the benzene ring. Structure II is more stable than III:



When Cl^- reacts with PS, HCl is formed. There will, however, be a dilution effect on the concentration of HCl present in the degrading polymer at any time in the presence of PS, and this will slow down the rate of dehydrochlorination of PVC. Thus the presence of PS will have a stabilizing effect on PVC.

Figure 8(a-f) shows the variation in mechanical properties as a function of percentage composition and time. Fig. 8(a, f) shows the dependence of ultimate tensile strength on % composition at two different times, i.e., at 0 h and at 500 h of natural weathering. It can be seen that PVC has greater tensile strength than PS. The values of tensile strengths for the different compositions fall within those for the pure polymers. So as far as tensile strength is concerned, the blends are less superior to the pure polymers. It can also be seen that, for any composition, an increase in tensile strength is obtained with increase in time of outdoor exposure. Figure 8(c, d) shows the dependence of % elongation on composition at two different periods. PVC has a greater extensibility than PS. The percentage elongation was found to decrease with increase in exposure time for all the blends. Figure 8(e, f) shows the dependence of Young's modulus on percentage composition of the blends at 0 hr and at 500 h of exposure. Again all values of modulus for the various ratios of PVC/PS fall within those for the pure polymers. However, at any composition of the blend, the modulus increases with increase in time of exposure. It could be concluded that on long exposure both the tensile strength and modulus increase with time of outdoor exposure while the elongation decreases. It was also seen from the spectra studies mentioned earlier on that the polymers degraded with increase in time of exposure.

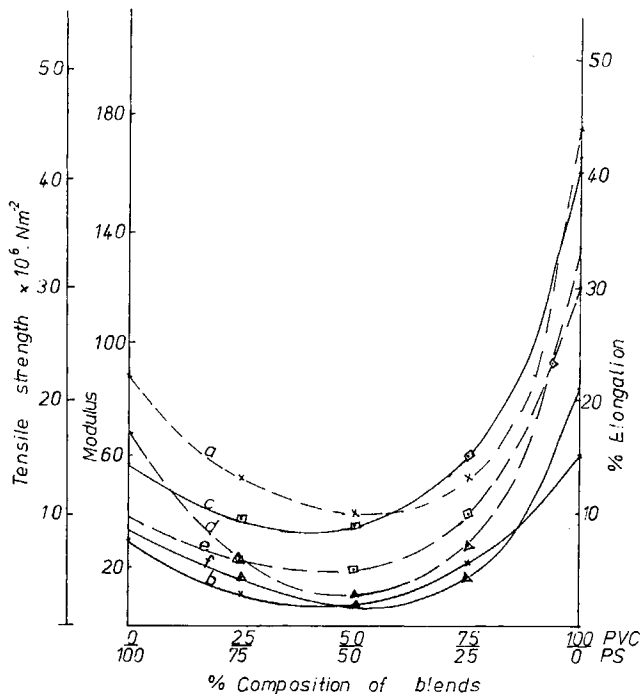
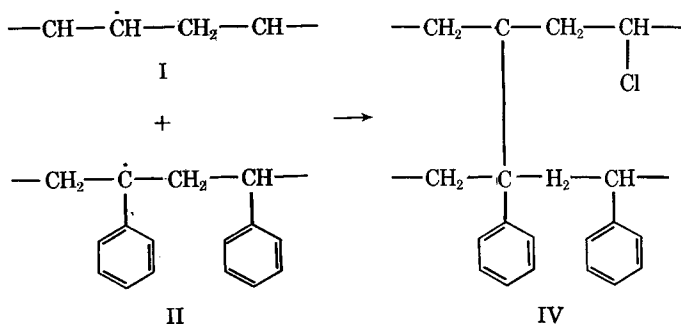


Fig. 8. Natural weathering of PS/PVC blends. Dependence of mechanical properties on percentage composition at two different times. The full lines represent data of 0 h, while the broken lines represent the data after 500 h of exposure. Each property measured is represented by the same symbol. (x) (a, b) Tensile strength; (□) (c, d) % elongation; (Δ) (e, f) modulus.

In all cases the observed mechanical properties go through a pronounced minimum which is considerably lower in magnitude than observed for the pure components. Comparison of these properties of the blends with the pure components should be done with caution. The minimum in Figure 8 is more or less symmetrical about 50:50 composition. These high values for pure components exist because the samples neck and cold-draw. Most of the blends do not neck but break somewhere in the vicinity of the yield point, generally where the stress goes through a maximum. It should be pointed out, however, that necking and cold-drawing is not ordinarily a usable property of an end product, so it may not reflect a serious material limitation unless cold-drawing will be required during fabrication. Therefore, while numerically the reduction in percentage elongation, tensile strength, and modulus by blending is quite large, it should be seen to represent more the loss of a phenomenon at a particular temperature rather than a continual diminution of property. As a matter of fact, all these properties are seen to increase with longer exposure times. This observed rigidity may be due to formation of crosslinks between the macroradicals produced during degradation. Macroradicals I and II come together to form crosslinked networks, i.e.,



In order to prove the theory of the observed chemical crosslink formation of the chains, we then studied this by measuring the selective solubility of the blends in a good solvent for one of them. In the case of 50:50 PS/PVC the gels formed became insoluble in chlorobenzene whereas PVC is 100% soluble. Scott and co-workers¹⁷ have also shown in recent work that low-density polyethylene and PVC do form crosslinked gels which also became insoluble in dichloromethane, which is also a good solvent for PVC.

Blends of Polystyrene (PS) and Polybutadiene (PB)

The presence of PB in PS has been studied with a view to knowing how the presence of either of the polymers affects the weatherability of the other as a result of exposure outdoors in our environment when the daily temperature ranged between 25°C and 37°C and the atmospheric conditions varied through dry and cold weather to hot and humid and to hot and wet. The polymer samples have also been heated in an air oven at 100°C.

The degradability of the polyblends have been followed by measuring the changes occurring in the mechanical properties using an Instron machine. The IR spectra were used to follow the changes occurring in the microstructure.

From the stress-strain curves obtained for the polymers and their blends, it is seen that pure PB shows the creep effect. The graph for PB is typically that of a soft and tough polymer. Very low value was obtained for the modulus, confirming that it is a soft polymer. Figure 9 provides a summary of the mechanical properties for these blends. Each of these properties had been carefully examined in relation to variation in composition of the blends and the time for outdoor exposure or heating. Figure 9 (a,b,c) shows the plot of ultimate tensile strength, modulus, and percent elongation against composition of the blends, respectively, at 500 h of exposure, while Figure 9(d,e,f) shows the plot of the ultimate tensile strength, modulus, and % elongation against composition, respectively, at 0 h.

In this system, variation in these properties is monotonic, showing no maximum or minimum. Figure 9(c, f) shows the plot of % elongation at 0 h and 500 h, respectively, against composition of the blends. It is seen that the elongation increases with increase in the amount of PB in the blend. Generally the materials lost their extensibilities fairly rapidly on aging. Pure PB decreased from 800% elongation at 0 h to about 30% elongation after 500 h of exposure. The loss in elongation is accompanied by changes in other properties. Both the yield strength and the modulus increased considerably after 500 h of exposure. There is much improvement in their rigidity and toughness with aging. The area under the stress-strain curves decreased considerably also meaning that the impact

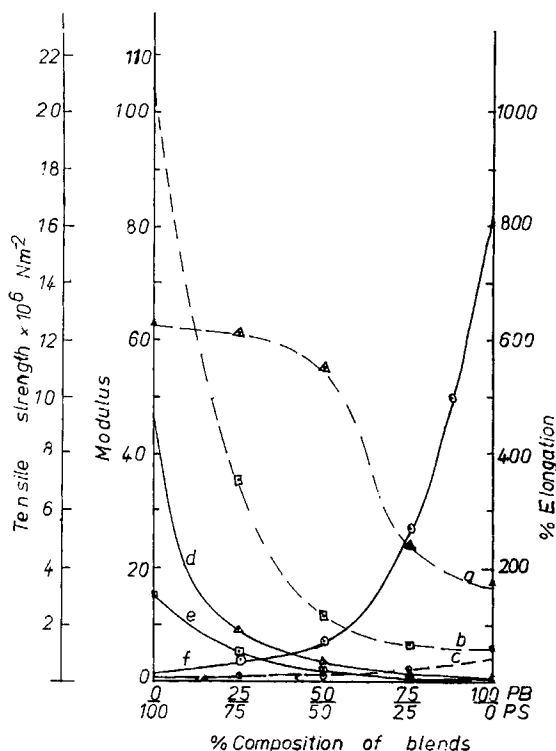


Fig. 9. Natural weathering of PS/PB lends. Dependence of mechanical properties on percentage composition at two different times. The full lines represent data at 0 hr while the broken lines represent the data after 500 h of exposure. Each property measured is represented by the same symbol. (Δ) (a, d) Tensile strength; (\square) (b, e) modulus; (\odot) (c, f) % elongation.

strength may be reduced. The more nearly additive elongation of the blend after irradiation is illustrative of the superior properties of the blends in terms of rigidity. Figure 9 (b,e) shows a rapid fall followed by a plateau starting at about 50:50 composition. This observation will have an important economic consequence in that to get a greatly improved combined mechanical properties, the optimum rubber content should not exceed 50% of the blend. Therefore, based on these observations, PB should be an effective blend for improving the toughness of PS.

It was also observed that the polyblends became hardened and thickened on long exposure or heating. This observation plus the increased rigidity obtained from reduced elongation may result from crosslinking formation. When PB is irradiated by UV light (either natural or artificial), it readily produces macroradicals and crosslinks readily form from loss of unsaturation.¹⁸ Hydroperoxides could readily form from degrading PB.¹⁹ These hydroperoxides could readily abstract hydrogen atoms, from the surrounding PS to give polystyryl radicals. These will increase the number of macroradicals present in the blends and since they are in each other's environment the possibility of forming crosslinkages is enhanced. There are three ways where by crosslinks could be formed, viz. (i) crosslinks between PB radicals could be formed, (ii) crosslinks between a PB radical and polystyryl radical, or (iii) crosslinks between two polystyryl radicals. The polymer gel which remained after degradation became insoluble in toluene (see Scheme 1). The macroradicals (a) can come together and form crosslinks, and this will account for the increased modulus observed for pure polystyrene. Similarly, the radical (b) can unite with radical (a) to form crosslinked gels, and again this will account for the increased rigidity of the blends. The carbonyl (c) can form crosslinks under UV irradiation. This will also account for the increased modulus of PB with exposure time.

Oven Aging

Infrared spectroscopy has been used to monitor the chemical changes taking place in the blends. The growth of the hydroxyl band appearing around 3450 cm^{-1} , the growth of the carbonyl peak at 1720 cm^{-1} , and the decay of carbon-carbon double bonds at 965 cm^{-1} have been followed. It is very well established that PB is very susceptible to oxidative degradation, i.e., deterioration of its physical properties due to chain scission, crosslinking, etc., because of the unsaturation present in all its structural units. Both the thermal and photooxidative processes have been widely studied,^{18,19} but these oxidative processes in the environment of another polymer have not found much mention in the literature. Figure 10 shows the dependence of hydroxyl index on heating time. It is seen here that both PS and PB show induction periods of 175 and 150 h, respectively, after which catalytic oxidation sets in the case of PB and gradual oxidation in the case of PS. However, no induction period was observed for the blends. In all cases, the OH index rises to a peak and then falls off.

Figure 11 shows the plot of carbonyl index against heating time for the various blends. It has been stated earlier that PS does not show appreciable increases in the relevant peaks before it brittled so that degradation of the blends will be monitored chiefly by the degradation of PB. It should also be pointed out that

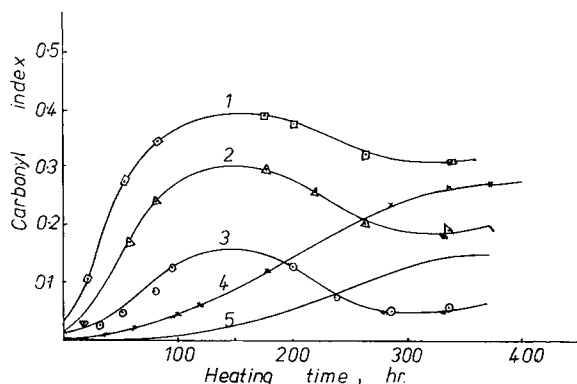


Fig. 11. Thermal oxidation of PS/PB blends. Dependence of carbonyl index upon heating times in air at 100°C. Composition of the blends: (1) 100% PB; (2) 75% PB/25% PS; (3) 25% PB/75% PS; (4) 50% PB/50% PS; (5) 100% PS.

a measure of carbonyl index is a better judgment of degradation than a measure of the OH index.¹⁶ It is seen that none of the blends shows any induction period. The rapid rise of these curves followed by a gentle fall could be of significance. The rapid rise will represent period of catalytic degradation. The gentle fall will mean that there is some stabilization of the blends taking place. This will probably happen if some of the products of degradation in PB diffuse within the blend and act as inhibitors. The blend containing 50:50 ratio PB/PS appears to be the most stable of the blends. This will have an important economic consequence in that where high impact and tolerance of heat is required the use of a 50:50 blend of PS/PB will be of a great advantage. The presence of PS in the blends helps to improve the thermal performance of PB.

Outdoor Weathering

Films of similar compositions as above have been exposed outdoors to be degraded by UV light radiating from the sun. Figure 12 shows the results obtained from the measurement of the carbonyl index as a function of time of exposure.

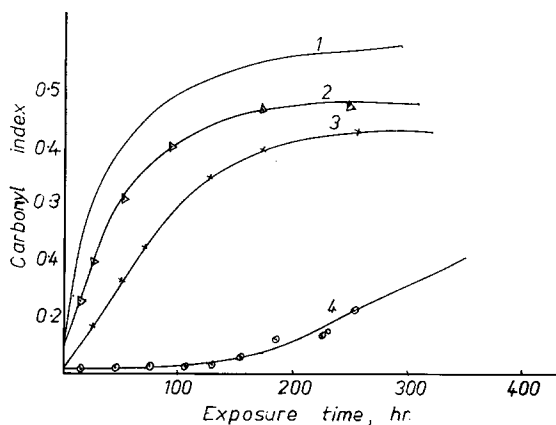


Fig. 12. Natural weathering of PS/PB blends. Dependence of carbonyl index upon time of outdoor exposure. (1) 100% PB; (2) 75% PB/25% PS; (3) 50% PB/50% PS; (4) 100% PS.

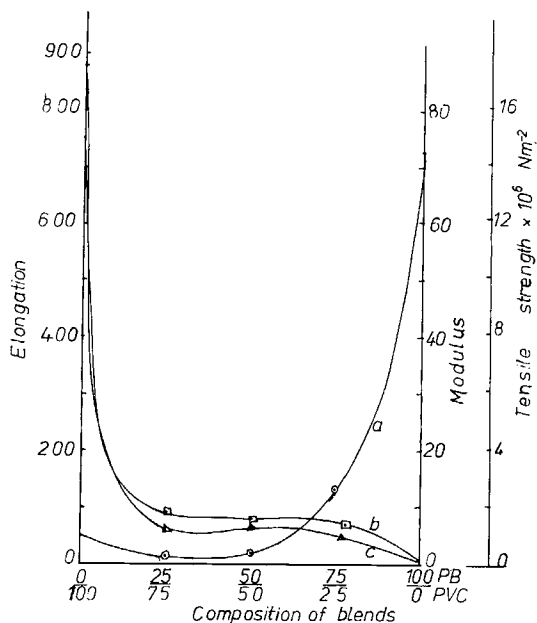


Fig. 13. Natural weathering of PB/PVC blends. Dependence of (a) elongation at break, (b) ultimate tensile strength, (c) modulus, on percentage composition of the blends.

These exposures have been done at various times of the year, and the general pattern of the curves are the same. It is interesting to note that none of the polyblends show any induction period due to the presence of PB which is highly susceptible to photooxidation. The carbonyl index rises steeply to a peak and then is followed by a plateau. It is observed that the region where the curves level off corresponds to the period when thickening of the films occurred, as observed in the mechanical properties. There is no corresponding leveling off in the case of PS alone. We did not observe any growth in the conjugated carbonyl peak at 1685 cm^{-1} whereas there exists dominant development in the saturated carbonyl at 1720 cm^{-1} . This observation has been associated with the crosslinking reaction usually resulting from β -scission of the alkoxy radical.

Blends of Poly(vinyl Chloride) (PVC) with Polybutadiene (PB)

Poly(vinyl chloride) is a polymer of high commercial importance, and it is known to degrade on irradiation by UV light on heating. Kolawole and co-workers²⁰ have recently examined the blend of PVC with ABS when exposed to tropical conditions and have shown that PVC helps to impart stability onto ABS. In the present study the effect of PVC on PB and vice-versa had been studied when the polyblends were exposed outdoors. We have also examined the changes in the mechanical properties of the blends. The results obtained have been presented in Figures 13–15.

Figure 13(a,b,c) shows the plot of percentage elongation at break, ultimate tensile strength, and modulus against composition, respectively. It is seen that, as PB is added to PVC, the curve first decreases to a minimum at about 30% of added PB and thereafter the elongation increases with addition of PB. On the

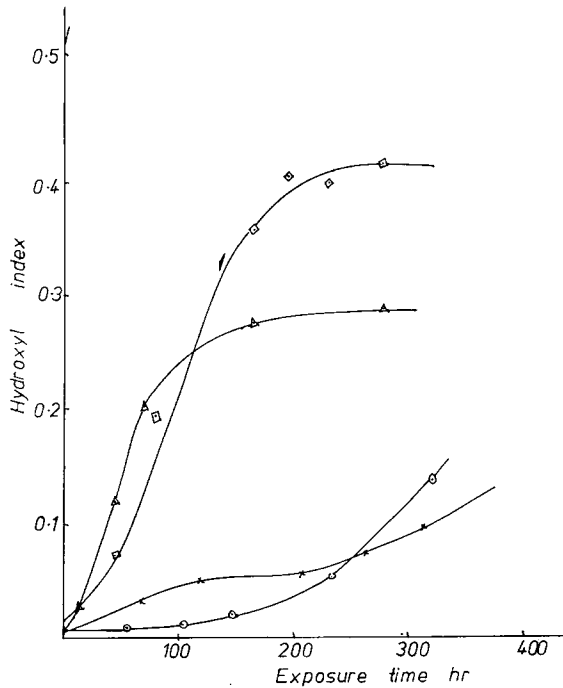


Fig. 14. Natural weathering of PB/PVC blends. Dependence of hydroxyl index upon outdoor exposure time. (□) 100% PB; (Δ) 75% PB/25% PVC; (×) 50% PB/50% PVC; (○) 100% PVC.

other hand, as PVC is added to PB, both the ultimate tensile strength and modulus increase gradually and then are followed by a plateau. The fall in elongation between 0:100 to 25:75 PVC/PB, is compensated for by the tremendous increase in ultimate tensile strength and modulus. Similarly the very rapid

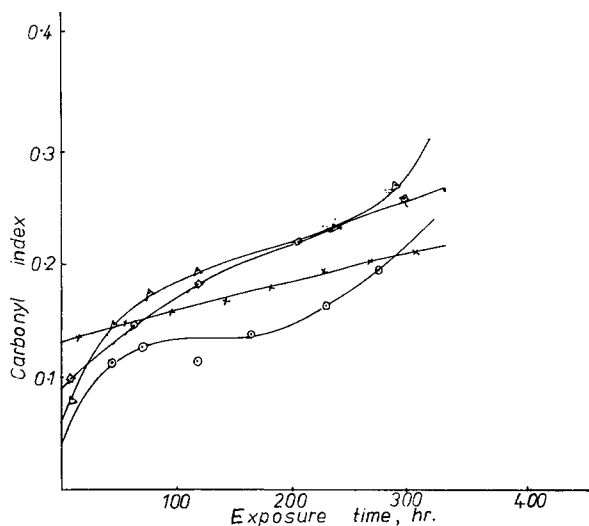


Fig. 15. Natural weathering of PB/PVC blends. A plot of carbonyl index against outdoor exposure times. (○) 100% PVC; (×) 50% PVC/50% PB; (Δ) 75% PB/25% PVC; (□) 25% PB/75% PVC.

rise in % elongation beyond 60:40 PB/PVC is accompanied by a fall in the ultimate tensile strength and modulus. However, in the regional around the minimum for elongation, a plateau is observed for the ultimate tensile strength and modulus. Again it was found that for the blends containing PB, the films became thick and hard on long exposure. It was also found that the elongation decreased with exposure or heating time. There were corresponding increases in the ultimate tensile strength and modulus.

We have used the infrared spectra to monitor the degradation taking place in the microstructure. Unsaturated carbonyl peaks were observed at 1620 cm^{-1} , 1665 cm^{-1} , and 1685 cm^{-1} while a saturated carbonyl peak was observed at 1720 cm^{-1} . The development of the peak at 1720 cm^{-1} was followed to estimate the rate of degradation. The development of the hydroxyl peak converging at 3450 cm^{-1} was similarly followed. It should be pointed out that both polymers when degraded will give the peaks mentioned above so that the growth observed comes as a result of the simultaneous degradation of both polymers. But since PB is more vulnerable to UV attack than PVC, it is likely that degradation of the blend will be started by breakdown of PB.

Figure 14 shows the dependence of OH index on the time of outdoor exposure. Similar graphs have been obtained for oven aging. In each case, the graph rises rapidly until a peak is reached. None of the blends has an induction period, and only PVC which is not as susceptible to oxidation as PB has an induction period of about 150 h. Figure 15 shows the dependence of carbonyl formation at the time of outdoor exposure. These graphs do not follow any particular order. If the rate of change of slope is used as a measure of rate of degradation, then there is usually an initial rapid photooxidation, which is followed by autoretardation. The blend containing 50:50 composition seems to degrade gradually and looks to be the most stable of all the blends. The time when the blends entered the autoretardation stage corresponds to the time when the films became thickened and hard and the time gel formation appeared, which was characterized by its insolubility.

References

1. S. Krause, in *Polymer Blends* D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. 1.
2. I. C. McNeill, in *Developments in Polymer Degradation*, N. Grassie, Ed., Applied Science, London, 1977, Vol. 1.
3. Y. Mizutari, S. Matsuoka, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **38**, 2045 (1965).
4. I. C. McNeill, in *Developments of Polymer Degradation*, N. Grassie, Ed., Applied Science, 1977, Vol. 1, p. 181.
5. A. Jamieson and I. C. McNeill, *J. Polym. Sci.*, **14**, 603 (1976).
6. N. Grassie and W. H. B. Leeming, *Eur. Polym. J.*, **11**, 819 (1975).
7. A. Jamieson and I. C. McNeill, *J. Polym. Sci.*, **12**, 387 (1974).
8. A. Jamieson and I. C. McNeill, *J. Polym. Sci.*, **14**, 1839 (1976).
9. I. C. McNeill, L. Ackerman, and S. N. Gupta, *J. Polym. Sci.*, **16**, 2169 (1978).
10. I. C. McNeill and D. Neil, *Eur. Polym. J.*, **6**, 569 (1970).
11. R. E. Robertson and D. R. Paul, *Polym. Eng. Sci.*, **12**, 157 (1972).
12. R. E. Robertson and D. R. Paul, *J. Appl. Polym. Sci.*, **17**, 2579 (1973).
13. J. G. Henniker, *Infrared Spectroscopy of Industrial Polymers*, Academic, New York, 1967, p. 51.
14. B. Dodson and I. C. McNeill, *J. Polym. Sci.*, **14**, 353 (1974).
15. E. G. Kolawole and G. Scott, *J. Appl. Polym. Sci.*, **26**, 2581 (1981).
16. E. G. Kolawole and J. B. Adeniyi, *Eur. Polym. J.*, to appear.

17. G. Scott, private communications.
18. S. W. Bevan and D. Phillips, *Eur. Polym. J.*, **10**, 593 (1974).
19. G. Scott and M. Tahan, *Eur. Polym. J.*, **13**, 981 (1977).
20. E. G. Kolawole, G. E. Mbamali, and J. Y. Olayemi, *J. Appl. Polym. Sci.*, **25**, 2133 (1980).

Received April 9, 1981

Accepted December 10, 1981

Corrected proofs received May 3, 1982