

NATURAL WEATHERING, PHOTO- AND THERMAL OXIDATION OF THE TWO-PHASE SYSTEM POLYISOBUTYLENE AND POLY(METHYL METHACRYLATE)

E. G. KOLAWOLE

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

(Received 10 June 1983; in revised form 28 September 1983)

Abstract—Blends of polyisobutylene (PIB) and poly(methyl methacrylate) (PMMA) covering the entire composition range have been examined by subjecting them to natural weathering, thermal oxidation and photooxidation. By i.r. analysis, viscometry and Instron testing, interaction between the two polymers was discovered. The blend of 20:80 PIB-PMMA gave the best mechanical performance. I.R. analysis indicated that the degradation of the blends led to enhancement of the interaction between the two polymers giving the blends improved resistance against oxidation. The blend of 20:80 PIB-PMMA proved to be the most stable against heat and light. PIB and PMMA degrade by a chain scission mechanism as indicated by changes in molecular weight.

INTRODUCTION

There is considerable interest in polymer blends for obtaining new materials having desirable physical properties of the various constituents; consequently, considerable interest has been shown in the physical properties of polymer blends. Recent reviews [1-3] list many references to the very considerable literature on this subject. Blending of polymers often leads to new products which may exhibit useful mechanical, chemical and thermal properties. Addition of elastomers has often been used to improve toughness and environmental degradation [4]. Physical blends of a rubber and a polymer, as well as various types of copolymer systems, are of commercial interest, e.g. ABS and impact modified polystyrenes. It should be noted that addition of rubber to a polymer does not necessarily lead to improvement in mechanical properties. In some cases there is considerable improvement in chemical resistance and resistance to other degradative agents [5]. Considerable attention has been paid to thermal degradation of polymers using TVA as a tool for polymer characterisation [6] whereas relatively little attention has been paid to changes in chemical property during thermal oxidation and natural weathering.

Two-phase systems consisting of PMMA with a second polymer have been studied for many years [1-3, 6-7] but most attention has been paid to compatibility and thermal degradation. In the present study, attempts have been made to modify the mechanical and chemical properties by blending with polyisobutylene. It is desirable to know about the stability of the polymers and their blends under very hot and humid conditions. It is also desirable to know of any influence of these blends on the thermal oxidation and photooxidative stability of PMMA. Krause [8] reported that PIB-PMMA is an incompatible blend but our study of the mechanical properties of the blend indicated some interactions. This work will extend the literature on this blend, determining

the extent of compatibility and examining its effect on molecular breakdown of the polymers in the presence of each other.

EXPERIMENTAL

Materials

The polymers used in this work are poly(methyl methacrylate) (PMMA) $\bar{M}_n = 63.2 \times 10^3$, supplied by RAPRA and polyisobutylene (PIB) of medium molecular weight $\bar{M}_n = 1.40 \times 10^6$, supplied by Aldrich Chemical Coy Ltd. All the other solvents of analytical grade were supplied by British Drug Houses Ltd.

Preparation of films

A series of 11 films with compositions PMMA-PIB: 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90, 0:100 was prepared. Films were cast from 2% solutions containing both polymers onto a clean Hg surface in a desiccator. Tetrahydrofuran was the solvent used for all the solutions. An atmosphere of N_2 at reduced pressure was maintained for 48 hr. The films were finally dried to constant weight *in vacuo* at room temperature. Light micrographs of the films show that the elastomer is present as separate spherical droplets in a matrix of PMMA. The size of the droplets varies over the very wide range of about 10-150 μm .

General degradation techniques

Method of thermal oxidation. Accelerated thermal oxidation of the films were carried out by mounting the sample films on specially prepared cardboard holders and were hung in the Wallace air oven. Each sample film was contained in a separate cavity. The temperature of the test was 100°. Degradation was followed by recording i.r. spectra at regular intervals. The development of relevant peaks indicated the rate and nature of degradation.

Method of natural weathering. Natural weathering of the films was carried out by exposing the films in open air at the geographical experimental station of Ahmadu Bello University, Zaria, Nigeria on latitude 11° north and longitude 7.5° east. Films were mounted on specially prepared holders. Films of uniform thickness of 0.20 mm were used for the carbonyl and hydroxyl group measurements. For the mechanical properties, film samples of $5.0 \times 0.7 \times 0.02 \text{ cm}^3$

were used. The mechanical properties of the films were compared using the Instron Testing Machine Model TM-M at 25°. Outdoor weathering was carried out between July 1980 and June 1982.

Viscosity measurement. Values of the limiting viscosity number $[\eta]$ of the degraded and undegraded polymers were determined in appropriate solvents as a function of heating time.

Ultraviolet degradation. Gallenkamp u.v. equipment emitting in the range 300–365 nm was used. The test films were irradiated at 35° and the degradation was followed by recording the i.r. spectrum at regular intervals.

Embrittlement test. Probably the final assessment of the extent of degradation in polymer and polymer blend films is the embrittlement test. The test samples were bent through an angle of 180°. Crumbling and flaking indicate embrittlement.

RESULTS AND DISCUSSION

The stability of PMMA–PIB 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 outdoor exposure time, heating in an air oven and u.v. irradiation.

Outdoor exposure

(i) **Mechanical property study.** Experiments were carried out with PMMA–PIB blends covering the whole range of compositions in order to investigate the mechanical and chemical behaviour of the undegraded and degraded samples.

Figure 1 (a–f) summarizes the mechanical properties studied. Attention has been directed on the relationships between tensile strength, elongation and modulus and their dependence on composition of the blends and weathering time. Figure 1 (c and d) shows the dependence of tensile strength on composition at

two different times, *viz.* 0 hr and after 720 hr of natural weathering. It is evident that PMMA has greater tensile strength than PIB. It can also be seen that the tensile strength increases up to a maximum and then falls off. Maximum tensile strength is obtained for a blend of 20:80 PIB–PMMA. From the 50:50 blend, the curve flattens out. It can also be seen that, for any composition, an increase in tensile strength is obtained with increase in outdoor exposure time. Figure 1 (e and f) shows the dependence of Young's Modulus on composition of the blends at 0 hr and after 720 hr. Again the modulus is seen to rise to a peak, followed by a decrease as the amount of PIB in the blend increases. The peak is obtained at 20% PIB. At any composition, the modulus also increases with increase in exposure time, i.e. the resistance to brittleness increases and reaches a maximum at 20% PIB. Figure 1 (a and b) shows the dependence of elongation on time of exposure and blend composition. Elongation increases with increase in the content of PIB in the blend. It should be noted that, between blend compositions 10:90 and 30:70 PIB–PMMA, no increase in elongation is observed with increase in the proportion of PIB. It is also worth noting that it is in this region that maxima are obtained for tensile strength and modulus. It should be noted that, at any composition, the elongation decreases with increase in time of exposure. Thus, as degradation takes place, there is considerable improvement in the tensile and modulus properties. The observed improved rigidity comes as a result of a reduction in elongation.

That a maximum is obtained in some of the mechanical properties of the blends is suggestive of some interaction between the components. Also the increases in the values of tensile strength and modulus as weathering progresses suggest that this inter-

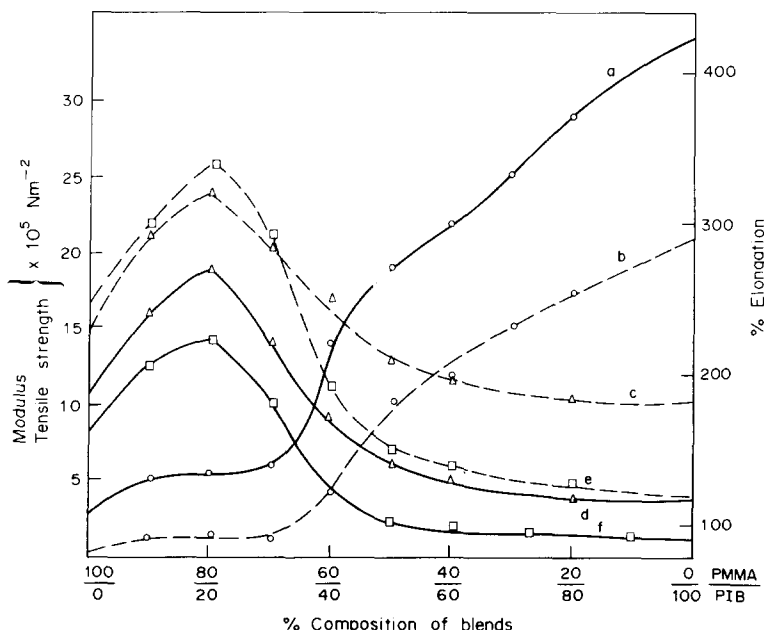


Fig. 1. Natural weathering of PMMA–PIB blends. Dependence of mechanical properties on blend composition at various times. The full lines represent the data for 0 hr; the broken lines represent data for 720 hr. (○) (a and b) % elongation. (△) (c and d) tensile strength. (□) (e and f) modulus.

action increases as degradation progresses. However, one would have expected a minimum in the elongation when maxima occur in tensile strength and modulus, but actually a plateau is reached. One could say that the plateau obtained in the elongation indicates that in this region the polymer chains become stiffer. This observation could be explained in several ways. The maxima could arise as a result of crosslinking between the polymeric chains due to interchain interactions of macroradicals. Another explanation centres on the fact that PMMA has a bulky methyl ester side-group and the isobutylene $-\text{C}(\text{CH}_3)_2-$ group is also bulky, so when PMMA is present in high proportion the bulkiness of the side-groups might hinder elongation of PIB. It has been reported by Kennedy [9] that PIB cannot act as a plasticiser for PVC because of the bulkiness of the side-groups. Also, Scott and coworkers [10] observed that, among a group of olefinic rubbers, PIB has the least segmental mobility. Thus it might be suggested that, as a result of the inability of PIB to plasticise PMMA and because of its low segmental mobility at low and ordinary temperatures, the observed plateau in the elongation is not unusual. Thus the observed maximum in the mechanical properties is a combination of the effects stated above (including intermolecular interactions). This is in agreement with the conclusion of Paul [11] that elongation at break of a polymer is a complex function of composition and this property is always diminished by blending. From 30:70 PIB-PMMA down to 100% PIB, the increase in elongation and consequent decrease in tensile and modulus properties are expected to be due to increase in chain flexibility as the amount of PMMA in the blend decreases.

The above blends were also heated in the Wallace air oven and the measurement of mechanical properties were repeated. The same trends as observed for outdoor weathering were obtained except that the reaction reached completion sooner.

(ii) *Chemical property study.* Apart from the studies made on mechanical properties, the changes in the microstructure using i.r. spectroscopy have been monitored. During outdoor weathering of the blends, developments of the carbonyl group at 1720 cm^{-1} , the hydroxyl/hydroperoxide group at 3450 cm^{-1} have been followed. For the moment, attention is directed to the carbonyl growth which has been used as a measure of degradation. The contributing factors to environmental degradation include solar u.v. and the heat of the sun. These factors may give a synergistic effect on the degradation of the blends.

Figure 2 shows the plot of carbonyl index as a function of outdoor exposure time for the blends and the homopolymers. Pure PMMA shows no development in carbonyl but this does not imply that it is not degraded [12]. PIB on the other hand shows an induction period of 50 hr after which the polymer is auto-oxidised. A maximum induction period of 250 hr was obtained with the 80:20 PMMA-PIB blend. The 60:40 blend has an induction period of about 100 hr. All other blends with high proportions of PIB exhibit no induction periods, i.e. weathering begins as soon as the films were exposed. For the blends having high PIB content, the carbonyl production rises to a maximum and followed by a fall until

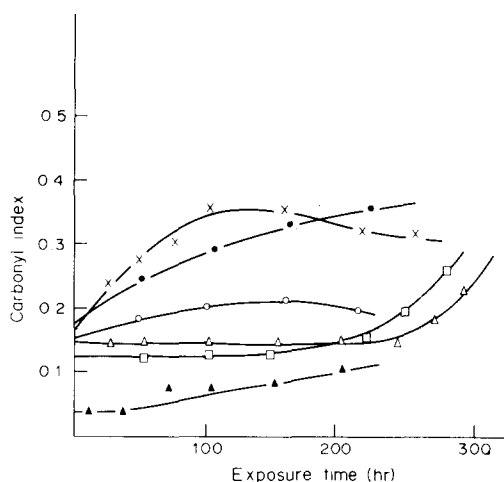


Fig. 2. Natural weathering of PMMA-PIB blends. Dependence of carbonyl index upon outdoor exposure time. (x) 60% PIB-40% PMMA; (□) 40% PIB-60% PMMA; (△) 20% PIB-80% PMMA; (○) 80% PIB-20% PMMA; (●) 50% PIB-50% PMMA; (▲) PIB.

the films break. It appears that there are two stages of degradation, an initial fast stage being followed by a slow stage. From the degradation patterns of the homopolymers, it is suggested that the initial fast stage is due to the oxidation of the rubber phase and the second slow stage is due to the degradation of PMMA. It is also concluded that the 80:20 PMMA-PIB is the most stable of all the blends to natural weathering, explaining the best mechanical properties.

Thermal oxidation

It has been found previously [13] that PMMA does not show any appreciable growth in the carbonyl index and therefore the development of hydroxyl index has been used to monitor the degradation of the blends during thermal oxidation in the Wallace oven.

Figure 3 shows the dependence of hydroxyl index upon heating time for PMMA and its blend with PIB. PMMA has an induction period of about 80 hr and an embrittlement time of about 100 hr. PIB has an induction period of 40 hr. On blending the period increased to a maximum of 200 hr with the 20:80 PIB-PMMA blend. The induction period decreases progressively to 150 hr at the 50:50 blend. At other compositions having PIB content $>50\%$, no induction period was obtained. Thus we see that the induction period is a measure of comparative stability of the blends. A general conclusion is that, when the PIB content is $<50\%$, PIB protects PMMA against thermal oxidation. Maximum protection is achieved at 20:80 PIB-PMMA. On the other hand, a small amount of PMMA in a PIB environment does not offer any protection to the blend.

In an attempt to discover the possible degradation mechanism, the viscosities of the degraded PMMA and PIB were measured as a function of heating time. No gels were formed. Figure 4 shows that the limiting viscosity number $[\eta]$ decreases with increase in heating time. The decrease in intrinsic viscosity and consequently molecular weight may be due to chain

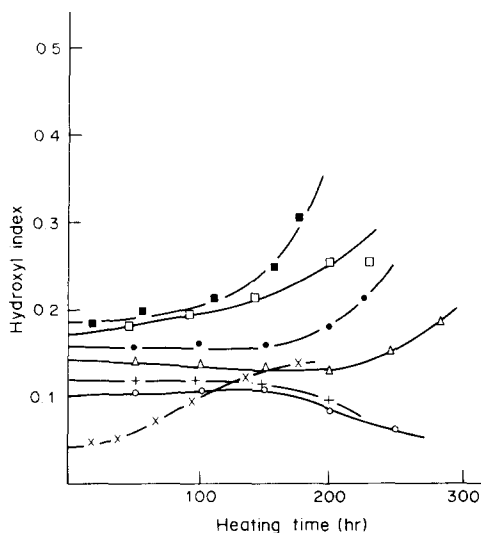
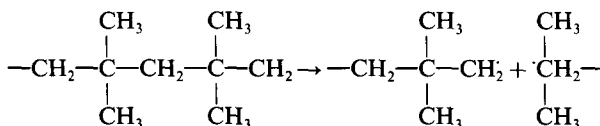
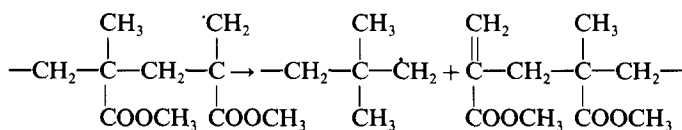


Fig. 3. Thermal oxidation of PMMA-PIB blends. Dependence of hydroxyl index upon heating time for various blends composition at 100°. (x) PIB; (o) PMMA; (+) 50% PIB-50% PMMA; (Δ) 20% PIB-80% PMMA; (\bullet) 40% PIB-60% PMMA; (\square) 80% PIB-20% PMMA; (\blacksquare) 60% PIB-40% PMMA.

scission or disproportionation reactions. In the case of PIB, disproportionation would lead to formation of one double bond per chain scission as found by Ranby and co-workers [14]. However, in the present work on thermal oxidation and natural weathering of PIB, an increase in unsaturation index was not found thus it is concluded that chain scission of the carbon-carbon bond in the main chain was responsible for the decrease in molecular weight.



In the case of PMMA, an increase in unsaturation index after an initial induction period was found. Thus chain scission with the formation of double bonds is the mode of degradation of PMMA. A macroradical is first formed as a result of heating and this macroradical undergoes chain scission with the formation of double bonds.



It was also observed that the films hardened on heating; this effect is probably due to the formation of crosslinks between PIB and PMMA radicals. It has been observed [15] that PMMA radicals show little tendency to form crosslinks because all the gels formed were soluble in THF. Also in this study the inability of PMMA and PIB to form stable crosslinks may be due to restriction in chain mobility which must be an important factor in recombination.

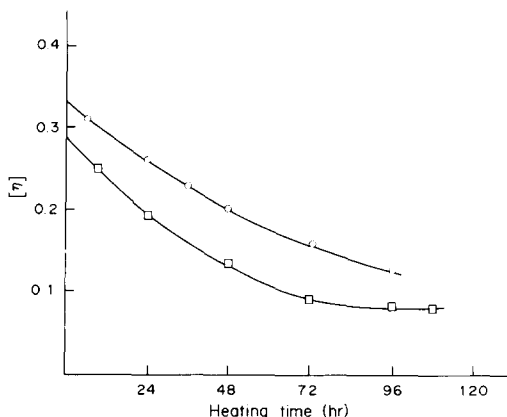


Fig. 4. Thermal degradation of PIB and PMMA. Dependence of limiting viscosity $[\eta]$ on time of heating in air at 100°. (o) PMMA; (\square) PIB.

Photooxidation of PMMA-PIB blends

Films with PIB-PMMA ratios of 0:100, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 100:0 were subjected to u.v. irradiation in air as described in the experimental section. The oxidation was followed by measuring the absorptions around 3450 cm^{-1} which may be attributed to hydroxyl and/or hydroperoxide groups and the bands at 1720 cm^{-1} due to carbonyl group. The carbonyl index has been used as a measure of oxidation.

Figure 5 shows the dependence of carbonyl index upon irradiation time. All blends containing up to 40% PIB exhibit induction periods. PIB has an induction period of about 50 hr; the blends 20:80 and 40:60 have induction periods of 400 and 150 hr

respectively. PMMA has no induction period. It can be concluded that PIB has a stabilizing effect on PMMA during u.v. irradiation. PIB has a similar effect on PVC [5]. It can thus be said that the structure of the blend formed during oxidation reac-

tions probably gives improved stability against light. The effect of ionizing radiation on the polymers have been extensively studied using various techniques with each author proposing different mechanisms [14, 16, 17]. Many of those studies were carried out *in vacuo* and the mechanism will be greatly altered when the polymers are mixed with another polymer and in the presence of oxygen. It has been established that

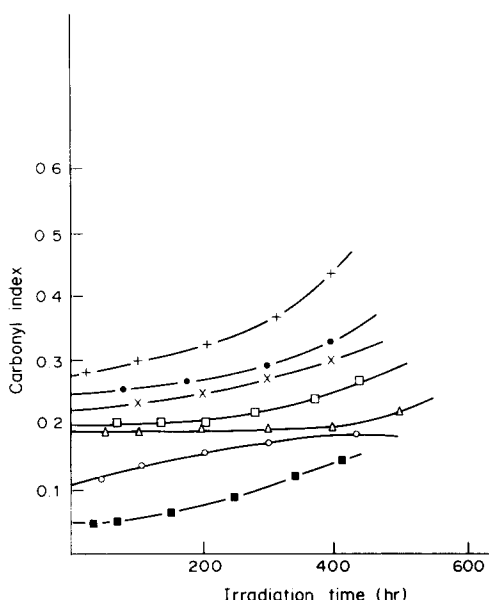


Fig. 5. Photodegradation of PMMA-PIB blends. Dependence of carbonyl growth on time of u.v. irradiation. (○) PMMA; (■) PIB; (+) 20% PMMA-80% PIB; (●) 40% PMMA-60% PIB; (×) 50% PMMA-50% PIB (□) 60% PMMA-40% PIB; (△) 80% PMMA-20% PIB.

photolysis of PMMA and PIB results in random scission of the polymer backbone [18]. Also from the present and previous studies [5], it has been established that chain scission is the mode of degradation for PMMA and PIB. However, in the presence of oxygen, formation of peroxy radicals and hydro-

peroxides must follow as indicated by the development of the bands at 3450 cm^{-1} .

REFERENCES

1. D. R. Paul and S. Newman (Eds), *Polymer Blends*, Vols 1 and 2. Academic Press, New York (1978).
2. S. L. Copper and G. M. Gates (Eds), *Adv. Chem. Ser. Am. chem. Soc.* **176** (1979).
3. O. Olabisi, L. M. Robson and T. M. Shaw (Eds), *Polymer-Polymer Miscibility*. Academic Press, New York (1979).
4. E. G. Kolawole and M. O. Agboola, *J. appl. Polym. Sci.* **27**, 2317 (1982).
5. E. G. Kolawole and P. O. Olugbemi, *J. appl. Polym. Sci.* In press.
6. I. C. McNeill, *Developments in Polymer Degradation Vol. 1* (Edited by N. Grassie). Applied Science, New York (1977).
7. I. C. McNeill, T. Straiton and P. Anderson, *J. Polym. Sci.* **18**, 2085 (1980).
8. S. Krause, *Polymer Blends, Vol. 1*. Academic Press, New York (1978).
9. J. P. Kennedy and N. G. Thame, *J. Polym. Sci. A1* **10**, 2507 (1972).
10. G. Scott, *Eur. Polym. J.* **13**, 989 (1977).
11. D. R. Paul, *Polymer Blends, Vol. 2* (Edited by D. R. Paul and S. Newman). Academic Press, New York (1978).
12. T. Avoja, M.Sc. Thesis, A.B.U. (1983).
13. E. G. Kolawole, *J. appl. Polym. Sci.* **27**, 3437 (1982).
14. P. Cartenson and B. Ranby, *Radiation Research*. North-Holland, Amsterdam (1967).
15. M. A. Bello, M.Sc. Thesis Ahmadu Bello University (1977).
16. E. N. Kurner, *J. Polym. Sci.* **2**, 1979 (1964).
17. J. P. Allison, *J. Polym. Sci.* **4**, 1209 (1966).
18. B. Ranby and J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilisation of Polymers*. Wiley, New York (1975).