

Further Experimental Evidences of the Compatibility of Poly(Vinyl Acetate) with Poly(Ethyl Methacrylate) and Its Dependence on the Ratio of the Molecular Weight of the Two Homopolymers

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Synopsis

Using various fractions of poly(ethyl methacrylate) (PEMA) and poly(vinyl acetate) (PVAc) of very narrow molecular weight distribution, a very wide range of 2–120 of molecular weight ratio \bar{M}_v PEMA/ \bar{M}_v PVAc, (\bar{M}_v)_r, was obtained. Studies of some tensile mechanical properties of films of the blends produced from solution on mercury confirmed strong dependence of the improvements of PVAc properties for blend with 18% PEMA on (\bar{M}_v)_r, especially in the range $5 \leq (\bar{M}_v)_r \leq 100$. The density of the films of the blend was much higher than those of the individual polymers and increased monotonically with (\bar{M}_v)_r. Optical micrographs of the films of the blends showed interactions between the two polymers with 18% PEMA composition, which appears to be more intimate as (\bar{M}_v)_r increases, as further evidence of compatibility and miscibility of the two polymers.

INTRODUCTION

The recent article of Olayemi and Ibiyeye¹ is one of the few reports on detailed study of the miscibility and compatibility of poly(vinyl acetate) (PVAc) with poly(ethyl methacrylate) (PEMA)—two polymers with relatively polar groups. The much earlier report by Van Eijnsbergen² on this polymer pair claimed their incompatibility apparently without proofs. Olayemi and Ibiyeye,¹ studying some mechanical properties of this pair of polymers separately and as blends, reported unambiguously the miscibility and compatibility of the polymers to be appreciable and dependent strongly on the ratio of the molecular weights of the two polymers (\bar{M}_v)_r. Using unfractionated polymer samples, they established that the best blend is produced with about 20% PEMA and 80% PVAc and a lower (\bar{M}_v)_r limit of about 5. An upper limit of about 100 was also speculated for (\bar{M}_v)_r.

One major reason for blending polymers together is to obtain a result which is superior in quality, e.g., mechanical, optical, stability and other qualities, to those of the individual homopolymers when fabricated. Each of these characteristics of a blend is studied, and the sum total of these qualities is considered for deciding the merits of compatible polymer pairs.

The work reported here is essentially an extension of that reported by Olayemi and Ibiyeye.¹ It critically examines some mechanical properties of

the blends from carefully fractionated homopolymers for any effects of molecular weight distribution on the previous result¹ and establishes the upper limit of $(\bar{M}_v)_r$. Studies on polymer density and microscopy are also reported and attempts have been made to account for the morphological variations accompanying blending of the two polymers.

EXPERIMENTAL

Materials

Poly(vinyl acetate) and PEMA samples were produced as described by Olayemi and Ibiyeye,¹ but using several different initiator and surfactant concentrations during the polymerizations in order to obtain polymer samples of very wide molecular weight variations. Each polymer sample prepared in this way was fractionated by the fractional precipitation method,³ using methanol-water and chloroform-methanol as solvent-nonsolvent pairs for PVAc and PEMA, respectively.

Polymer fractions of molecular weights $(\bar{M}_v)_r$ of $(0.40-2.01) \times 10^6$ for PVAc and $(0.89-4.98) \times 10^6$ for PEMA were obtained. The fractions were shown by some well-known methods^{3,4} to be of narrow molecular weight distribution. The various polymer fractions were used for our studies.

Chloroform, methanol, and other organic liquids employed were of the reagent grade obtained from the BDH Ltd., and purified by vacuum distillation prior to use.

Procedures

Blending, film casting, and mechanical property testing of films were carried out as described previously.¹ Film density (for pure homopolymers and their blends) was determined in a Davenport two-column density measuring apparatus serial no. DMD6 18/158 using water-KI media for the density gradient and a temperature of 23°C. The method in the instrument manual was followed.

An optical microscope Model LEIT Orthodux 2 Pol B₄ with camera and magnification of 25 was employed in producing micrographs from films of selected homopolymers and blends of different polymer composition and $(\bar{M}_v)_r$ values.

RESULTS AND DISCUSSION

Tensile Strength (TS), Initial Modulus (IM), and % Elongation (%E) of Blends

The previous report¹ relates to PVAc/PEMA blends of low values of $(\bar{M}_v)_r$, not exceeding 8, using unfractionated polymer samples. The results presented here cover a wide range of $(\bar{M}_v)_r$ value, from about 2 to 120, thus making it easy for one to recognize fully the pattern of the dependence of TS, IM, and %E on $(\bar{M}_v)_r$ of the polymers in the blends.

As the previous paper¹ fully described the variations of TS, IM, and %E of the blend of PVAc/PEMA on blend composition, all that has been presented

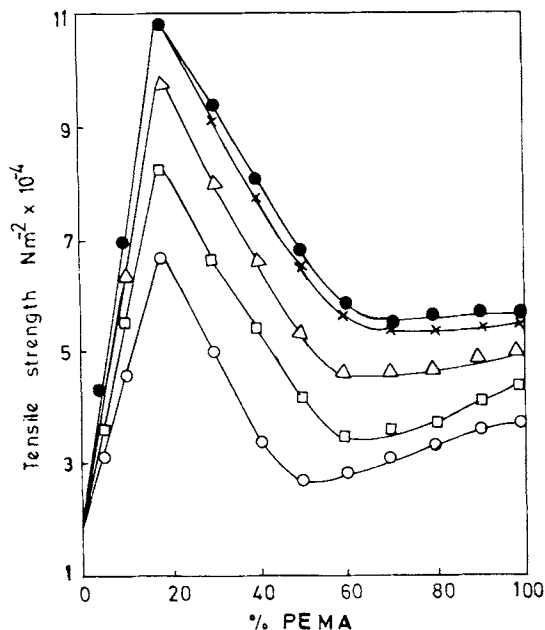


Fig. 1. Variation of tensile strength of PVAc-PEMA blends with composition, for PVAc of $(\bar{M}_v) = 0.041 \times 10^6$ and PEMA of (\bar{M}_v) of: (○) 0.89×10^6 ; (□) 1.95×10^6 ; (△) 2.98×10^6 ; (×) 4.32×10^6 ; (●) 4.48×10^6 .

here is a sample of similar curves representing the results for much wider and higher values of $(\bar{M}_v)_r$ for polymer samples of narrower molecular weight distribution.

Figure 1 shows plots of TS of the blends vs. blend composition. Figure 2 shows variation of IM with blend composition, while Figure 3 represents pattern for %E. A range of $(\bar{M}_v)_r$ of 22-109 was covered in each case. The full study, however, covers $(\bar{M}_v)_r$ of $\approx 2-120$. For each mechanical property studied, a maximum was observed at about 18-20% PEMA, in agreement with the previous report.¹ At higher values of $(\bar{M}_v)_r$, however, the position of the minimum, which was generally at about 40% PEMA for low values of $(\bar{M}_v)_r$, shifted toward higher values of % PEMA as $(\bar{M}_v)_r$ increased. This indicates that if a minimum is regarded as representing blend composition for maximum phase separation to occur, then blends with high values of $(\bar{M}_v)_r$ would tolerate much higher % PEMA without appreciable phase separation exhibited. Also, there were no regions of the property-composition curves, Figures 1 and 2 below the straight line joining pure PVAc property to that of a given pure PEMA used to produce the blend, i.e., the phenomenon of antagonism might be assumed to be absent in such blends. However, in spite of the absence of antagonism, the nearer the curve approaches the connecting straight line, the higher the chances of independent behavior of molecules of the two polymers blended, and hence the greater the chances of phase separation.

The particularly large increases in the TS of both polymers due to blending to 18% PEMA are worth noting. Increase in TS of PVAc or PEMA is a useful measure of blend quality. Since only as little as 18% PEMA was found to cause the largest change in the TS of the two polymers, it was considered

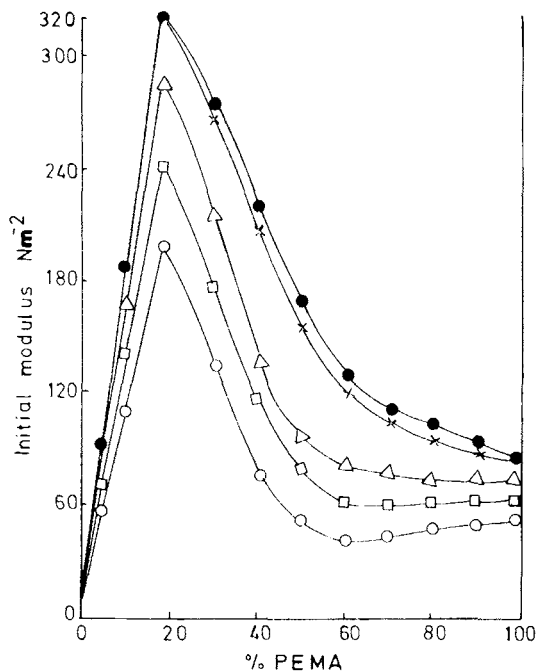


Fig. 2. Variation of initial modulus of PVAc-PEMA blends with composition, for PVAc of $(\bar{M}_v)_r = 0.041 \times 10^6$ and PEMA of $(\bar{M}_v)_r$ of: (○) 0.89×10^6 ; (□) 1.95×10^6 ; (△) 2.98×10^6 ; (×) 4.32×10^6 ; (●) 4.48×10^6 .

logical to evaluate the effect of $(\bar{M}_v)_r$ on TS, IM, and %E of blends containing this percentage of PEMA, (Figs. 4-6) and, generally on the basis of its effects on the properties of PVAc, the main component of the blend.

Figures 1 and 2 show large increases in TS and IM with % PEMA composition in the blends. The increase in TS or IM of PVAc caused by 18% PEMA in the blend composition itself increased with $(\bar{M}_v)_r$ to a limit at $(\bar{M}_v)_r$ around 100. Values of $(\bar{M}_v)_r$ much higher than 100 appear to affect only the pure PEMA side of the plots, i.e., increasing $(\bar{M}_v)_r$ no longer affects TS and IM of PVAc provided that % PEMA ≤ 18 .

Figures 4-6 summarize the effect of blending of 18 parts of PEMA with 82 parts of PVAc (w/w) on TS (Fig. 4), IM (Fig. 5), and %E (Fig. 6) for PVAc of different molecular weights. The plots relate the maximum increase produced by 18% PEMA in the various properties of PVAc to the molecular weight ratio $(\bar{M}_v)_r$. Figure 4 shows three sections, each essentially linear. At low $(\bar{M}_v)_r$ values, TS increased rapidly with $(\bar{M}_v)_r$ until at about $(\bar{M}_v)_r$ of 5 when the rate of increase of TS further increased linearly with $(\bar{M}_v)_r$ until $(\bar{M}_v)_r$ of about 100, when TS appeared constant with further increases in $(\bar{M}_v)_r$. A similar pattern of dependence of IM of PVAc on $(\bar{M}_v)_r$ was observed, except that the first change in slope occurred at about $(\bar{M}_v)_r$ of 20 rather than 5 observed for TS.

Equations have been calculated using the data of the linear portions of the TS and IM plots (Figs. 4 and 5, respectively). These equations are given in terms of $\Delta(\text{TS})_{\text{PVAc}}$ and $\Delta(\text{IM})_{\text{PVAc}}$, i.e., increase in TS and IM of PVAc,

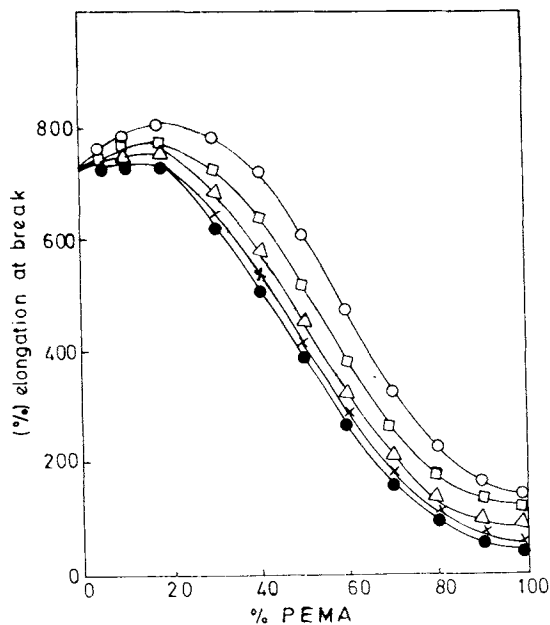


Fig. 3. Variation of % elongation of PVAc-PEMA blends with composition, for PVAc of $(\bar{M}_v) = 0.041 \times 10^6$ and PEMA of (\bar{M}_v) of: (○) 0.89×10^6 ; (□) 1.95×10^6 ; (△) 2.98×10^6 ; (×) 4.32×10^6 ; (●) 4.48×10^6 .

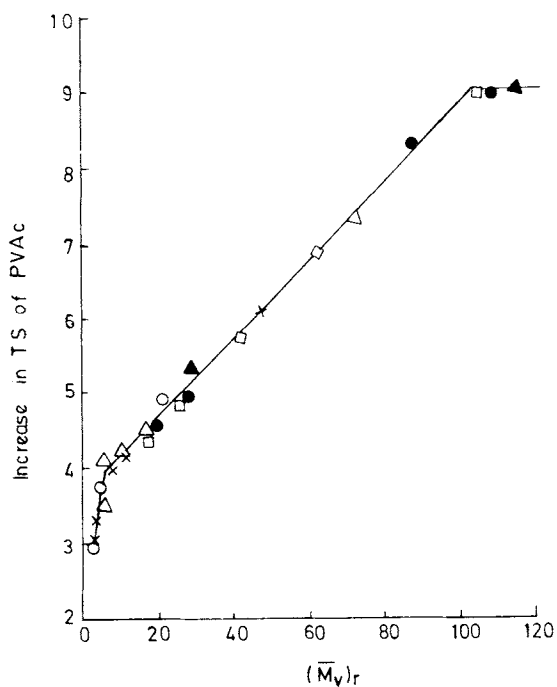


Fig. 4. Dependence of increase in tensile strength of PVAc produced by 18% PEMA in blend on $(\bar{M}_v)_r$.

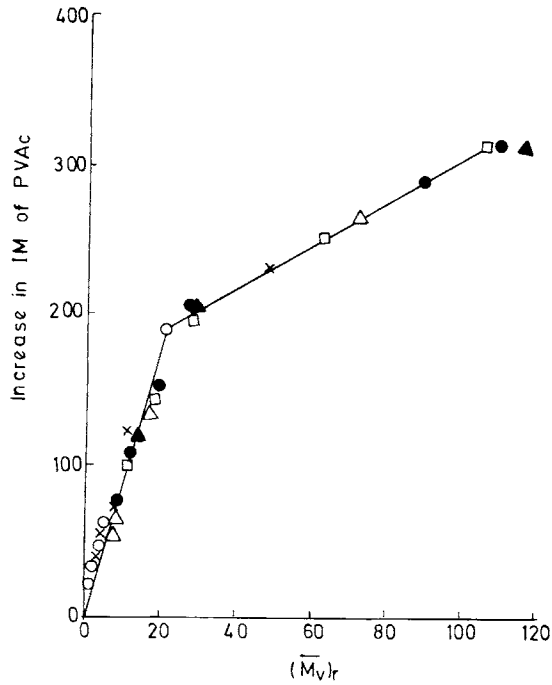


Fig. 5. Dependence of increase in initial modulus of PVAc produced by 18% PEMA in blend, on $(\bar{M}_v)_r$.

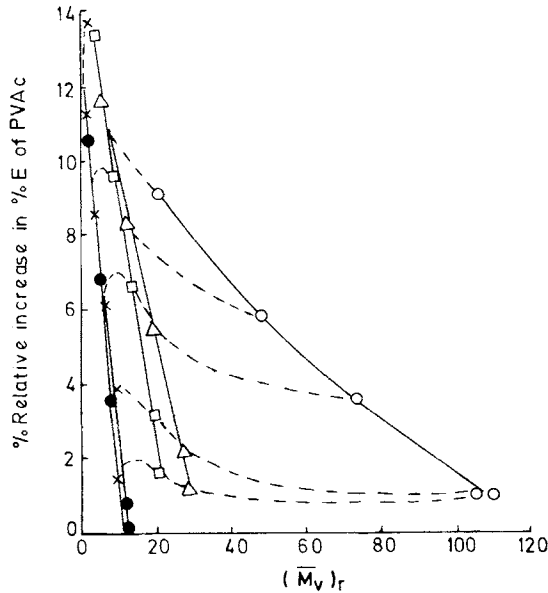


Fig. 6. Dependence of % relative increase in elongation of PVAc on $(\bar{M}_v)_r$ for PVAc fractions of $(\bar{M}_v)_r$ of: (○) 0.041×10^6 ; (Δ) 0.16×10^6 ; (□) 0.22×10^6 ; (●) 0.38×10^6 ; (×) 0.46×10^6 , blended with PEMA fractions of different values of $(\bar{M}_v)_r$ from 0.89×10^6 to 4.48×10^6 .

respectively, due to 18% PEMA as

$$\Delta(\text{TS})_{\text{PVAc}} = 3.7 \times 10^4 + 520(\bar{M}_v)_r \text{ (N m}^{-2}\text{)} \quad (1)$$

$$[\text{valid for } 5 \leq (\bar{M}_v)_r \leq 100]$$

$$\Delta(\text{IM})_{\text{PVAc}} = 160 + 1.44(\bar{M}_v)_r \text{ (N m}^{-2}\text{)} \quad (2)$$

$$[\text{valid for } 20 \leq (\bar{M}_v)_r \leq 100]$$

The corresponding equations for the % relative change, i.e., $\%(\Delta\text{TS})_{\text{rel}}$ and $\%(\Delta\text{IM})_{\text{rel}}$, respectively, in the properties of PVAc, plotted in Figures 4 and 5, expressed as percentage of the value for the pure PVAc are

$$(\Delta\text{TS})_{\text{rel}} = 200 + 3.33(\bar{M}_v)_r \quad (3)$$

$$[\text{valid for } 5 \leq (\bar{M}_v)_r \leq 100]$$

$$(\Delta\text{IM})_{\text{rel}} = 17 \times 10^2 + 17.33(\bar{M}_v)_r \quad (4)$$

$$[\text{valid for } 20 \leq (\bar{M}_v)_r \leq 100]$$

It was concluded from eqs. (1)–(4) that responses of TS and IM of PVAc in the blends of 82% PVAc–18% PEMA to $(\bar{M}_v)_r$ variations are different as demonstrated by differences in the lower limits of $(\bar{M}_v)_r$ for validity and the slopes of the straight line graphs.

From the relative increases in the properties of PVAc produced by presence of 18% PEMA, IM seems to be about five times as sensitive as TS to $(\bar{M}_v)_r$ variation. It is thus logical to recognize the range $20 \leq (\bar{M}_v)_r \leq 100$ as the most technologically useful for blending PEMA with PVAc in the ratio 18/82% by weight in order to produce very significant improvement to the mechanical, and possibly other properties of PVAc.

Figure 6 relates increases in %E of the PVAc samples to $(\bar{M}_v)_r$ for the blends of PVAc–PEMA of 18% (w/w) PEMA. Two sets of plots have been combined: (a) the effects of variations in $(\bar{M}_v)_r$ of PVAc on %E broken lines on one hand and (b) that produced by variations in $(\bar{M}_v)_r$ of PEMA on %E and how these are affected by $(\bar{M}_v)_r$ of the blends, respectively, by solid lines.

Percent relative increase in elongation of PVAc decreased essentially linearly with $(\bar{M}_v)_r$ for PVAc of relatively high molecular weights; a nonlinear decrease in this property with $(\bar{M}_v)_r$ has been observed. Generally the higher the molecular weight of the PVAc sample used, the faster the relative % increase in elongation of PVAc decreased with $(\bar{M}_v)_r$, as would be anticipated.

The curves in solid lines all show initial slight increase in relative %E with decrease in $(\bar{M}_v)_r$, each to a peak at an $(\bar{M}_v)_r$ value, which decreases with decreasing PEMA molecular weight. Each peak is followed by a sharp decrease in relative %E as $(\bar{M}_v)_r$ further decreases. These results indicate that PEMA samples of low molecular weight values are more effective in increasing relative %E of PVAc than those of the higher molecular weights. The broken

lines are linear for blends for PVAc of relatively higher molecular weight and show sharp decreases in %E of PVAc with increase in $(\bar{M}_v)_r$ of the 82% PVAc–18% PEMA blends, again suggesting that $(\bar{M}_v)_r$ should have moderate value.

Figures 4–6 therefore clearly establish the dependence of TS, IM, and %E of blends of PVAc–PEMA (82/18), w/w % on $(\bar{M}_v)_r$ as previously reported for much lower values of $(\bar{M}_v)_r$.

The upper limit of $(\bar{M}_v)_r$ value, i.e., $(\bar{M}_v)_{ru}$ probably represents the point of saturation of contact points or segments or interactions between PVAc and PEMA molecules as no further improvement in the mechanical properties was observed. At $(\bar{M}_v)_r \gg 100$ the plasticizing effect of PVAc on PEMA becomes pronounced; hence TS and IM of the blends might decrease with %E increasing accordingly. In understanding the blend system, it is appropriate to regard PVAc as the dispersing medium while PEMA is the dispersed phase in a solid solution of PEMA in PVAc.

Generally, PVAc demonstrates different levels of compatibility with at least 40% PEMA. This is the range of PEMA in PVAc–PEMA blend over which there is synergism (Figs. 1 and 2). The upper limit of PEMA for synergistic behavior increases above 40% with increase in $(\bar{M}_v)_r$. The peak of compatibility or maximum synergism is, however, always at about 18% PEMA and appears independent of $(\bar{M}_v)_r$.

Krause⁵ argued that compositional range of polymers for compatibility depends on the parameter χ_{AB} for polyA–polyB intermolecular interaction and $(\chi_{AB})_{or}$ their critical value. The parameter χ_{AB} is related to the enthalpy of interaction of the polymer repeat units and appears prominently in several early theoretical treatments of polymer solutions.^{6–9} According to Krause, the difference $\Delta\chi_{AB}$ between χ_{AB} and $(\chi_{AB})_{or}$ decreases as compositional range for compatibility increases. Hence our arguments and that of Krause taken together suggest that $\Delta\chi_{AB}$ and $(\bar{M}_v)_r$ are inversely related. Thus for a polymer pair to have a wide compositional range of compatibility, $\Delta\chi_{AB}$ is expected to be small while $(\bar{M}_v)_r$ should be reasonably large. The work reported here also clearly indicates that $(\bar{M}_v)_r$ has an upper limit, beyond which the observed compositional range of compatibility and $(\bar{M}_v)_r$ holds.

Polymer Blend Density

The density of each homopolymer did not show significant variations with molecular weight; hence the average of the experimentally determined values, i.e., 1.1905 and 1.1872, were employed for PVAc and PEMA, respectively. Densities of the blends are plotted in Figure 7 as a function of $(\bar{M}_v)_r$ for three types of blends of the same set of PEMA but three PVAc samples of different molecular weight values.

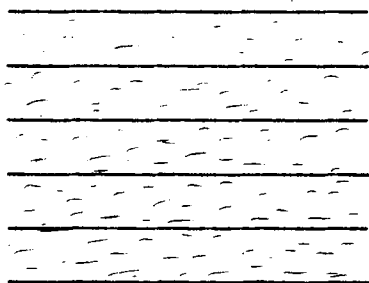
A straight line with a positive slope was obtained for each PVAc sample and five PEMA samples of different molecular weights. The slopes of the lines increase with decrease in the molecular weight of PVAc. Density of blend increased linearly with $(\bar{M}_v)_r$ in each case and is always higher than that calculated (1.1896) from the equation^{10–12} written with the assumption that incompatible polymers in a blend can be regarded to be independent and form two phases. For such a two-phase system, the density of the blend is related to

those of the two-polymer components and their respective weight fractions. It is known^{13,14} that density of a compatible blend is generally higher than that of an incompatible one from the same components, especially if the two components are homopolymers and have fairly simple repeating units.

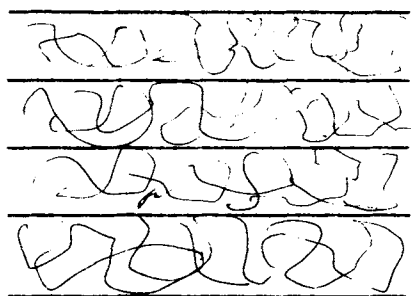
Our results indicate that, at about $(\bar{M}_v)_r$ of about 110, percent increase in blend density over what was expected on the basis of the assumption of incompatibility is about 5.5. This value compares very well with what some previous workers^{11,13,14} reported for very compatible blends especially those from components with polar groups.

Increase in density of blends above those values for the individual components might be attributable to presence of strong intermolecular interaction, mainly of the type polyA-polyB, leading to adhesion and, hence, improved molecular packing. According to Shur and Ranby,¹² the density of a compatible blend increases as level of compatibility of the two components increases.

The arrangements of PVAc molecules between those of PEMA below have been suggested to explain increases in the properties especially density of blend.



(i) Compact packing
 $(\bar{M}_v)_r \rightarrow 100$



(ii) Porous arrangement
 $(\bar{M}_v)_r \rightarrow 1$

The two cases represent PEMA molecules of the same molecular weight blended in (i) with PVAc of very low molecular weight i.e. $(\bar{M}_v)_r \rightarrow 100$ and in (ii) with PVAc of high molecular weight when $(\bar{M}_v)_r \rightarrow 1$. In model (i), the low molecular weight PVAc molecules align themselves regularly along the larger and essentially linear PEMA molecules. This arrangement favors a compact, oriented packing. It also allows easier formation of various types of bonds such as secondary bonds.¹⁵⁻¹⁸ In the second model, bonding would be more random and fewer and the film density smaller. Polymers with units that possess polar characteristics as in the case of acetate and methacrylate of PVAc and PEMA respectively, in mixed forms, are likely to undergo these various types of intramolecular interactions leading to changes in the properties of the individual homopolymers.

In both cases, however, the two polymers were well mixed, and demixing was not possible due probably to adsorption and/or adhesion of one polymer to the other, as suggested by previous workers.¹⁹⁻²² Where solvent is used for blending the two polymers, the mode of agitation of solution and rate of removal of solvent from the solution during evaporation could be important in deciding conformation of polymer molecules and hence segmental interactions

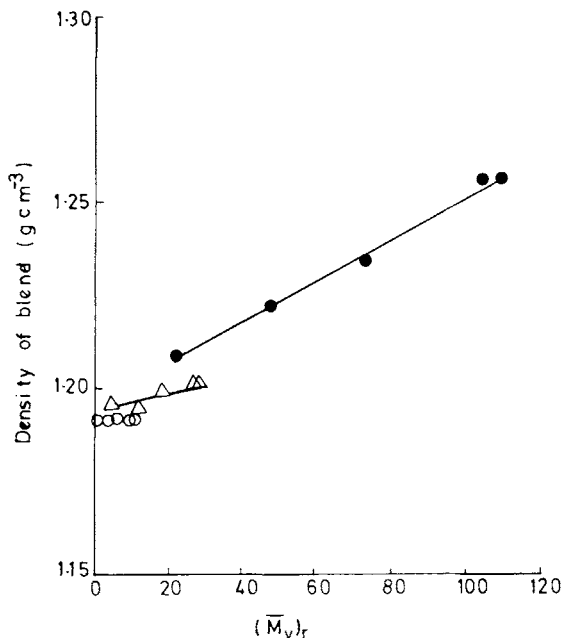


Fig. 7. Variation in density of PVAc-PEMA blends with $(\bar{M}_v)_r$ for 18% PEMA blend composition using PVAc of different $(\bar{M}_v)_r$ of: (○) 0.46×10^6 ; (△) 0.16×10^6 ; (●) 0.041×10^6 .

between the two components and consequently the extent of bond formation. Thus the results of this study support the earlier observation that the most compatible PVAc-PEMA blend is that containing 18% PEMA by weight, with a PVAc compound of reasonably low molecular weight and PEMA of high molecular weight such that $(\bar{M}_v)_r$ approaches 100.

Optical Microscopy

Films of blends of PVAc-PEMA of different % PEMA by weight were produced by the usual method of solution on mercury surface. Blends of different $(\bar{M}_v)_r$ values were produced and examined under the optical microscope. Only two sets of results representing two values of $(\bar{M}_v)_r$, i.e., 1.94 and 109.26, are produced here. Others, not shown, but with values of $(\bar{M}_v)_r$ intermediate between 1.94 and 109.26 have also been discussed. Micrographs are labeled as Figures 8-15.

Figures 8-11 are micrographs from blends with PVAc of fairly high molecular weight (0.46×10^6) and PEMA of low molecular weight (0.89×10^6), giving $(\bar{M}_v)_r$ value of 1.94 with different % PEMA, i.e., Figure 8 (18%), Figure 9 (40%), Figure 10 (80%), and Figure 11 (film of Figure 8 heated in air oven at 100°C for 1000 h). Figures 12-15 are results for corresponding sets of blends from PVAc of low molecular weight (0.041×10^6) matched with PEMA of high molecular weight, giving $(\bar{M}_v)_r$ of 109.26. The micrographs from the homopolymers are omitted as they show no unusual structures. A magnification of 25 was used in each case.

Generally, the micrographs show specific changes in the morphology of the blends with changes in blend composition and $(\bar{M}_v)_r$. Figures 8-10 and

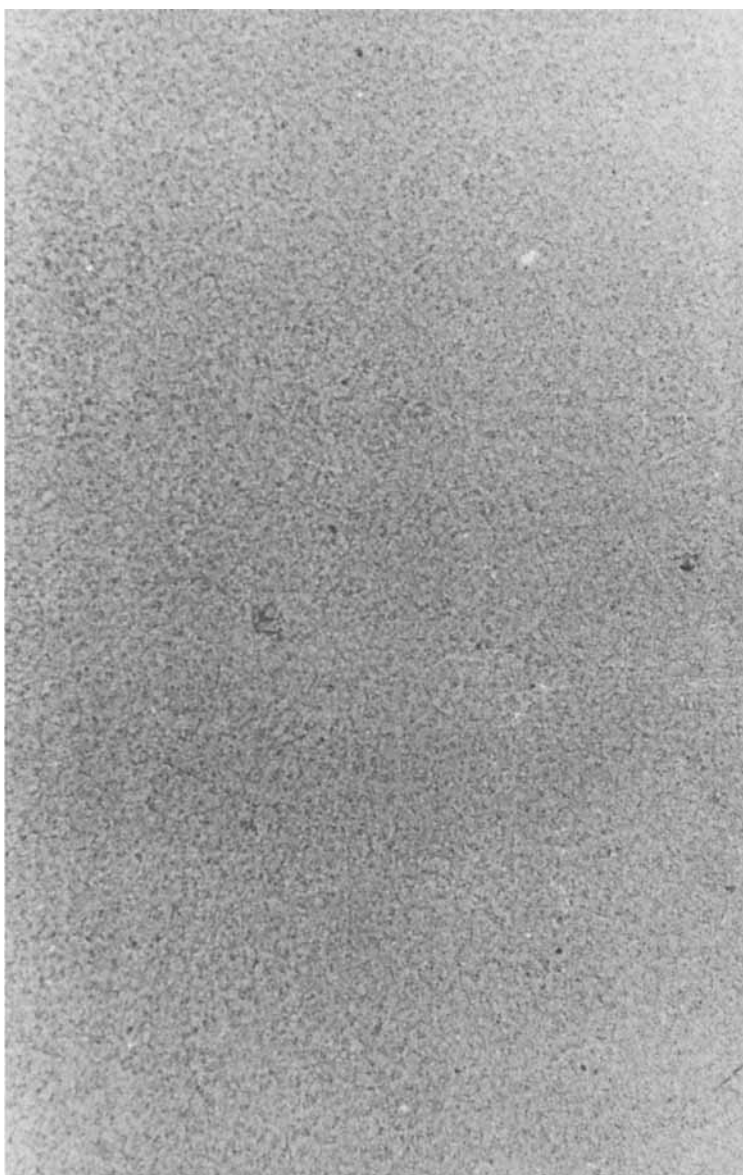


Fig. 8. Micrograph from PVAc of 0.46×10^6 and PEMA of 0.89×10^6 (18% PEMA) (magnification of 25).



Fig. 9. Micrograph from PVAc of 0.46×10^6 and PEMA of 0.89×10^6 (40% PEMA) (magnification of 25).

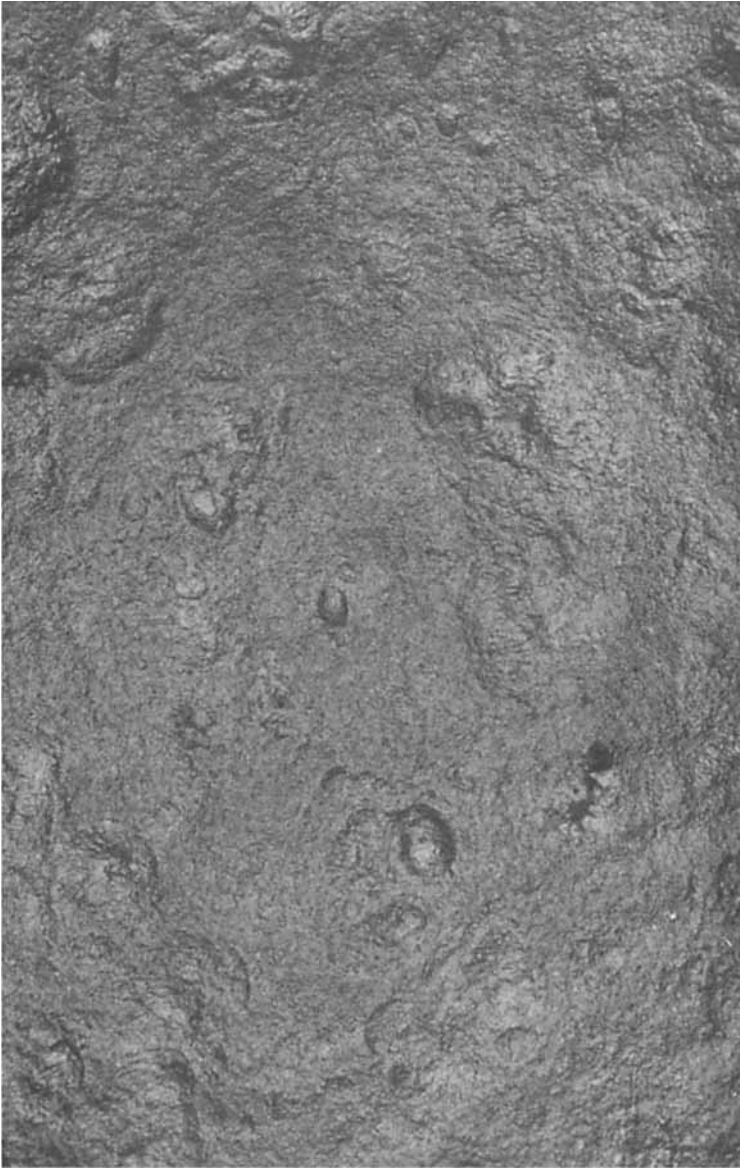


Fig. 10. Micrograph from PVAc of 0.46×10^6 and PEMA of 0.89×10^6 (80% PEMA) (magnification of 25).



Fig. 11. Micrograph from film used for Figure 8 heated in an air oven at 100°C for 1000 h (magnification of 25).

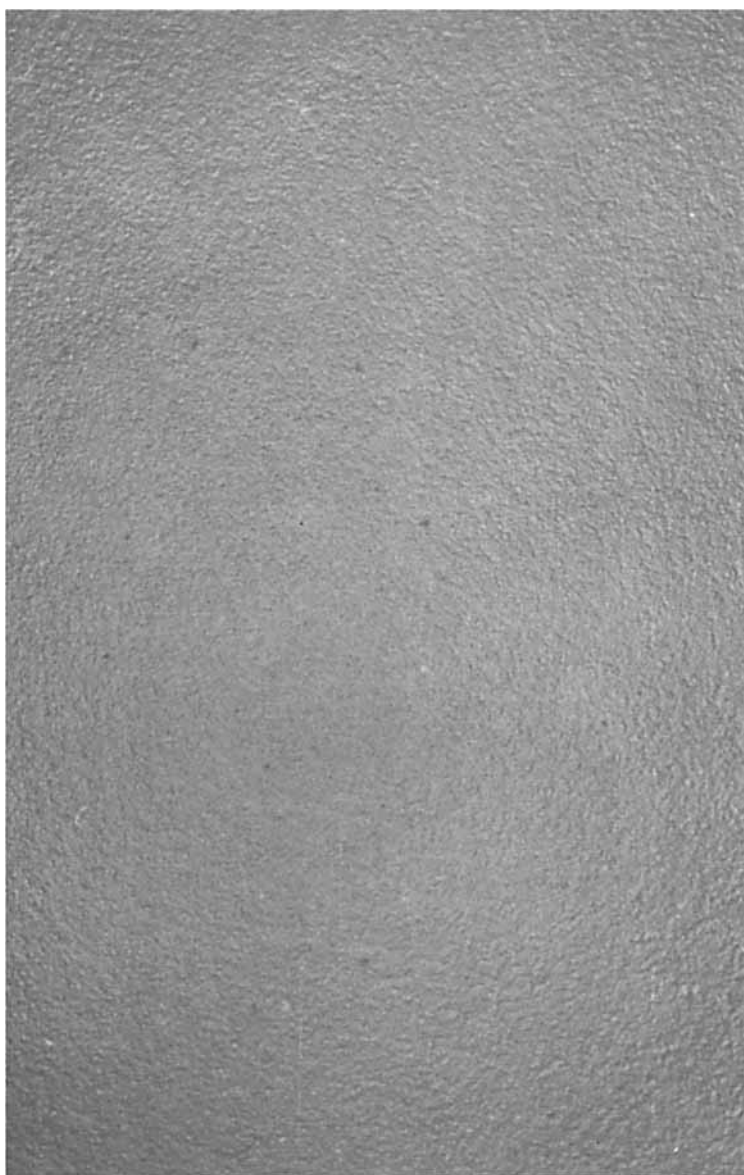


Fig. 12. Micrograph from PVAc of 0.041×10^6 and PEMA of 4.48×10^6 (18% PEMA) (magnification of 25).



Fig. 13. Micrograph from PVAc of 0.041×10^6 and PEMA of 4.48×10^6 (40% PEMA) (magnification of 25).



Fig. 14. Micrograph from PVAc of 0.041×10^6 and PEMA of 4.48×10^6 (80% PEMA) (magnification of 25).



Fig. 15. Micrograph from film used for Figure 12 heated in an air oven at 100°C for 1000 h (magnification of 25).

Figures 12–14 show that from somewhat homogeneous structure of pure PVAc (not shown) structural changes in blends pass through fine and homogeneous microstructure (Fig. 8) through one with clear phase separation and marked domains and phase boundaries at 40% PEMA (Fig. 9). Blends with 80% PEMA (Fig. 10) show micrographs which are finer and suffer much less phase separation than those with 40% PEMA. Figures 12, 13, and 14 follow the trend described for Figures 8, 9, and 10. The two sets of micrographs confirm the significance of blend composition and existence of highly compatible blend structure at 18% PEMA, and a clearly incompatible one with phase separation at about 40% PEMA.

Effect of Molecular Weight Ratio (\bar{M}_v)_r on Film Structure

Comparison of Figure 8 with 12 and Figure 9 with 13 confirms the importance of (\bar{M}_v)_r in the morphology. While Figures 8 and 12 are both from blends of 18% PEMA, Figure 12 with a much higher value of (\bar{M}_v)_r of 109.26 shows greater homogeneity and finer structure than that of Figure 8 for which (\bar{M}_v)_r is 1.94. This structural discrepancy is more pronounced with blends of 40% PEMA (Figs. 9 and 13) with (\bar{M}_v)_r of 1.95 and 109.26, respectively. The latter blend showed much less phase separation than the former, with domains still appearing, though less emphatically. Thus all our conclusions made so far about blends of PVAc–PEMA are corroborated that high (\bar{M}_v)_r values are required to produce highly compatible blends of 82/18 (w/w) PVAc/PEMA to provide significant increases in the mechanical and possibly other properties of the composite polymers.

As stated in the earlier section of this paper, and according to Patterson,²³ the type of solvent, the mode of solution agitation, and the rate and mode of removal of solvent from the solution during film casting are among the important factors deciding the morphologies of the blends. Nevertheless, the results of the study reported here for two values of (\bar{M}_v)_r clearly indicate the effect of (\bar{M}_v)_r on morphology, for the same set of conditions of film casting and composition of blend.

Although increase in (\bar{M}_v)_r of blend improves blend quality, it might not be experimentally possible to completely eliminate phase separation from the 60/40 (w/w) PVAc/PEMA blends by merely increasing (\bar{M}_v)_r as indicated by this study.

Thermal Stability of Blend

That blends of 18% PEMA (wt%) show thermal stability which depends on (\bar{M}_v)_r has been demonstrated by the structures of the micrographs of Figures 11 and 15, i.e., the films in Figures 10 and 12, each heated in the air oven at 100°C for 1000 h. Figure 11 indicates a much faster deterioration of the blend of (\bar{M}_v)_r of 1.94 than that of Figure 15 with (\bar{M}_v)_r of 109.26, both blends containing 18% PEMA. A detailed study on the thermal stability of various blends of PVAc–PEMA is in progress in our laboratory.

All the results reported in Figures 8–15 show clearly that molecular intermingling of the two polymers is very important at boundaries of polymer segments, thus causing adhesion or adsorption of polymers, probably through formation of mainly hydrogen bonds. There is a general change in the

properties of the blends which depends on the factors $(\bar{M}_v)_r$ and blend composition as has been established by our study and reported in this article.

Permeation by the flexible PVAc molecules of the more rigid PEMA molecules was possible, producing a discontinuity in the blend characteristics. Extent of discontinuity of blend structure would be expected to decrease with increase in the extent of permeation. It could therefore be understood why 18% PEMA blends with large values of $(\bar{M}_v)_r$ show little or no discontinuity and, on exposure at 100°C for 1000 h, did not appear to have suffered much structural deterioration. The principle of using extent of permeation for predicting the extent of discontinuity in polymer blend structure has been applied by other workers, including Huang and Lin,²⁴ Michaels et al.,²⁵ and Paul Ebra-Lima,²⁶ particularly for blends produced by melt mixing.

A lot of other interesting results have been observed in our study of blends of PVAc and PEMA, which show that there is a lot of promise in the technology into which our findings might be put, though the problem of melt mixing of the two polymers still has to be faced.

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