Blends of Poly(vinyl Acetate) and Poly(ethyl Methacrylate): Some Mechanical Properties

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Synopsis

Poly(vinyl acetate) (PVAc) and poly(ethyl methacrylate) (PEMA) were solution blended in chloroform and cast into films on mercury surface. Some mechanical properties of the films were studied with the Instron Testing Machine. Tensile strength (TS), initial modulus (IM) and elongation at break of the films were found to depend highly on blend composition, and increased above the values for the pure polymers, each showing a peak at about 20% PEMA. The peak values of TS, IM, and elongation at break depended on an important factor, $(\overline{M}_v)_r$, the ratio of the molecular weights of (PEMA) to (PVAc). Improvements to the mechanical properties of the polymers due to blending were considered to be as a result of the presence of favorable and strong (PVAc–PEMA) intermolecular interactions which reveal miscibility and compatibility of the polymers. A lower critical value $(\overline{M}_v)_r$ of 4.9 was found, above which no phase separation would be expected on blending these two polymers to the extent of 20% by weight of PEMA.

INTRODUCTION

Various thermodynamic parameters are considered in deciding whether two or more substances which are chemically related or unrelated would mix or unmix when they come together. These parameters include the solubility parameter, enthalpy, and entropy of mixing. They all add up to decide the free energy of mixing of the substances. The effects of these and other factors on polymer blending are extensively discussed in the two volumes of the books edited by Paul and Newman.[1] If polymeric, the macromolecular properties of the substances, such as size, configuration, and conformation affect these thermodynamic parameters and become extremely important in deciding miscibility of the substances. Where units within the polymeric structures of the molecules are similar e.g., polar or nonpolar, at least an additional interaction factor comes into play during and after mixing such substances.[2,3]

Compatibility of polymers on the macromolecular level can be defined as the ability of the substances to exist together, consequently forming a new system of improved characteristics, while their miscibility could be regarded as a mere ability to mix and inability to spontaneously unmix or produce phase separation.[4,5] Several other definitions for polymer compatibility and miscibility such as those due to Brydson[6] and Ambrose et al.[7] are known.

Blends of polyvinyl acetate (PVAc) with poly(ethyl methacrylate) (PEMA) have been studied. The effect of blending on some mechanical properties of films obtained from the solution in chloroform as common solvent for the polymers has been evaluated. The influence of the spread of the mo-

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lecular weights of the two polymers on quality of blends has been considered specifically in order to determine the extent to which the polymers are compatible and also the forces likely involved in the blends.

EXPERIMENTAL

Materials

Poly(vinyl acetate) and PEMA samples were produced in our laboratory by the emulsion polymerization method as modified and described by Ibiyeye.[8] Essentially, $K_2S_2O_8$ was used as the initiator with sodium lauryl sulpfate as emulsifier. Polymerization was carried out at various temperatures at a single emulsifier concentration below its critical micelles formation value. Appropriate variations in the polymerization conditions were made in order to obtain PVAc and PEMA samples of different viscosity average molecular weights as recorded in Table I.

Conversion to PVAc was generally about 75%, while to PEMA it was always close to 62% for the various samples. Our unpublished results indicate that the PEMA samples were of narrow molecular weight distribution.

Chloroform was a reagent grade chemical from the British Drugs Houses Ltd. (BDH) and used after purification by vacuum distillation.

Procedures: Blending and Testing

Solutions of each polymer sample of appropriate strengths, were made in chloroform. Appropriate volumes of the solutions of the two polymers, in pairs, were mixed to give homogeneous mixtures with the total polymer weight kept constant, while variations in the compositions of the blends were made, from 0 to 100% in PEMA.

Films of individual polymers, or their blends, were cast from solution, treated at 20°C and 65% RH, and tested for their mechanical properties as described by Olayemi and Adeyeye.[9] Film thicknesses of polymers were usually about 3×10^{-3} mm and an Instron Testing Machine (Model 1026) was employed for their testing using a strain rate of 50 mm min^{-1} through-

TABLE I
Molecular Weight Values of the Polymer Samples Studied

	$\overline{M} v \times 10^{-6}$
Poly(vinyl acetate)	
S_1	0.531
S_2	0.570
S_3	0.638
S_4	0.721
S_5	0.745
Poly(ethyl methacrylate)	
S_6	1.513
S_7	2.212
S_8	3.008
S_9	3.816

out. From the stress–strain curves the tensile strength, initial modulus, and elongation at break of the films were determined.

RESULTS AND DISCUSSION

Figure 1 showing the stress–strain curves for the PVAc and PEMA samples and some of their blends indicates that the somewhat rubbery soft and weak characteristics observed for PVAc gradually gave way to the hard and brittle characteristics of PEMA as the percentage of the latter was increased in the blend.

Figure 2 describes the dependence of tensile strength TS of films of the polymers on blend composition. Tensile strength shows an increase from that for PVAc to a peak, followed by a decrease to a minimum, then a final increase to the value for PEMA, with increase in percentage PEMA in the blend. Some areas above and below the additivity straight line joining $(TS)_{PVAc}$ to $(TS)_{PEMA}$ were observed. The area above, for a given pair of PVAc and PEMA increased while that below the line decreased with increase in $(\overline{M}_v)_r$, the ratio of the molecular weights $(\overline{M}_v)_{PEMA}/(\overline{M}_v)_{PVAc}$. Generally, the ratio (area above)/(area below) the additivity line increased with $(\overline{M}_v)_r$.

The position of $(TS)_{max}$ is always at about 20% PEMA, while the location of the minimum, in terms of % PEMA, increased with $(\overline{M}_v)_r$. The appearance of areas above the additivity line suggests synergistic (advantageous) behaviors while areas below indicate antagonistic (unfavorable) behaviors when these polymers are blended as described.

The variation of $(TS)_{max}$ with the viscosity average molecular weight $\overline{M}_v$ of PEMA is described in Figure 3. $(TS)_{max}$ increased with $(\overline{M}_v)_{PEMA}$ for each $(\overline{M}_v)_{PVAc}$ value in the manner shown. The curve occupying the lowest position was obtained for the highest $(\overline{M}_v)_{PVAc}$' while the curve at the top
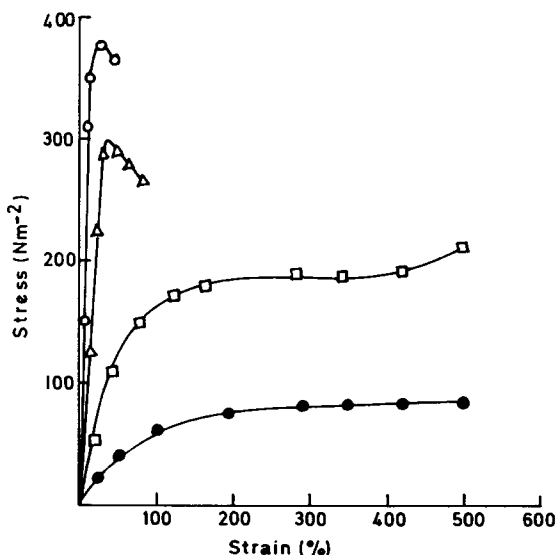

Fig. 1.   Stress–strain curves for PVAc/PEMA systems with $(\overline{M}_v)_{PVAc}$ of 0.721 × 10⁶ and $(\overline{M}_v)_{PEMA}$ of 3.816 × 10⁶. (●) PVAc; PEMA in blend: (□) 15%; (△) 80%; (○) 100%.
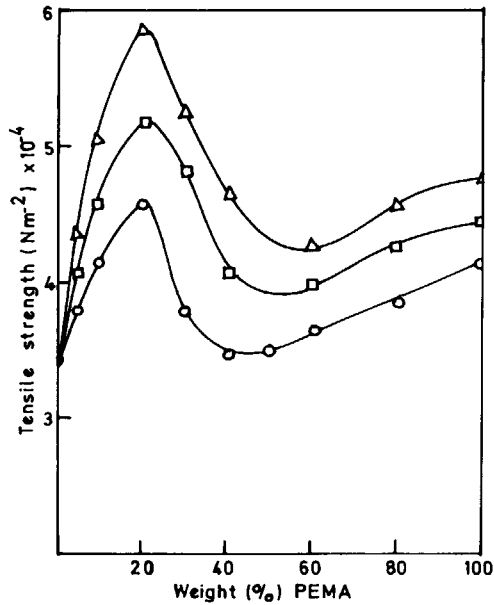
Fig. 2. Variation of TS with blend composition, for $(\overline{M}_v)_{\mathrm{PVAc}}$ of 0.570×10^6 and $(\overline{M}_v)_{\mathrm{PEMA}}$ $\times 10^6$ of: (○), 1.513; (□) 3.008; (△) 3.816.

represents the PVAc sample of lowest molecular weight. Thus $\Delta(\mathrm{TS})_{\mathrm{PVAc}}$ increased with $(\overline{M}_v)_r$ and $(\overline{M}_v)_{\mathrm{PEMA}}$.

Figure 4 shows the influence of $(\overline{M}_v)_{\mathrm{PVAc}}$ on $(\mathrm{TS})_{\max}$ for the blends. For large $(\overline{M}_v)_{\mathrm{PEMA}}$ values, $(\mathrm{TS})_{\max}$ decreased almost linearly with $(\overline{M}_v)_{\mathrm{PVAc}}$. However, for lower $(\overline{M}_v)_{\mathrm{PEMA}}$ values, decrease in $(\mathrm{TS})_{\max}$ is not pronounced and nonlinear, becoming more rapid with large molecular weight (PVAc) samples.
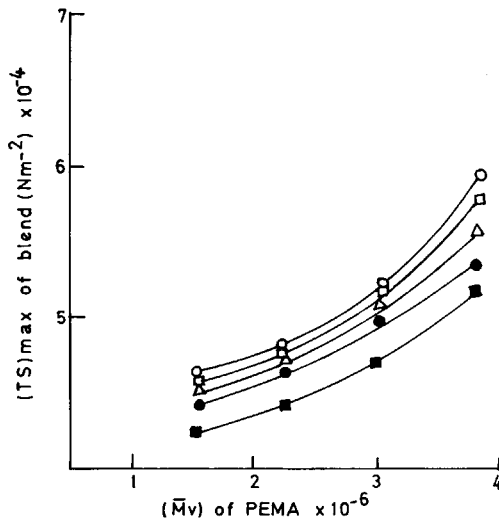

Fig. 3. Dependence of $(\mathrm{TS})_{\max}$ with $\overline{M}_v$ of PEMA for PVAc samples of $\overline{M}_v \times 10^6$ of: (○) 0.531; (□) 0.570; (△) 0.638; (●) 0.721; (□) 0.745.
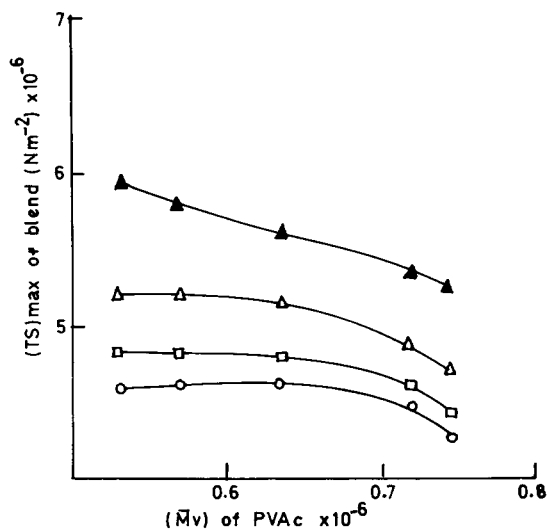
Fig. 4. Variation of $(TS)_{max}$ with $\overline{M}_v$ of PVAc for PEMA samples of $\overline{M}_v \times 10^6$ of: ($\bigcirc$) 1.513; ($\square$) 2.212; ($\triangle$) 3.008; ($\blacktriangle$) 3.816 ($\times 10^6$).

Figure 5 describes the dependence of % PEMA required for $(TS)_{max}$ and initial modulus maximum $(IM)_{max}$ on the molecular weight of PVAc. Both $(TS)_{max}$ and $(IM)_{max}$ behaved in the same way in the lower range of $(\overline{M}_v)_{PVAc}$ values. They remained at about 20% PEMA up to $(\overline{M}_v)_{PVAc}$ of about 0.65 $\times 10^6$. Both properties then dropped sharply, the $(TS)_{max}$ more rapidly than $(IM)_{max}$, showing that (TS) and (IM) of a polymer film may behave in different ways as previously reported.[9] These results show that it is advisable to work with low molecular weight PVAc samples, below $(\overline{M}_v)$ of about 0.65 $\times 10^6$
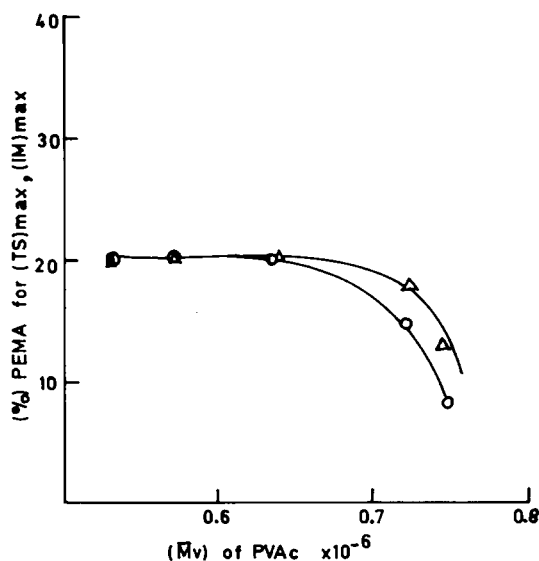

Fig. 5. Dependence of % PEMA required for $(TS)_{max}$ and $(IM)_{max}$ on $\overline{M}_v$ of PVAc: ($\bigcirc$) $(TS)_{max}$; ($\triangle$) $(IM)_{max}$.

in order to obtain blends that can tolerate up to 20% PEMA, especially as it is shown later that high molecular weight PVAc samples vs. high molecular weight PEMA samples, i.e., low $(\overline{M}_v)_r$ values, give smaller improvement to the TS and IM of either of the two polymers than high molecular weight PEMA samples taken against low molecular weight PVAc samples.

Figure 6 shows a rather complicated influence of $(\overline{M}_v)_r$ on the peak value of TS of the blends, for the four PEMA and five PVAc samples studied. Four separate curves were obtained for the four different PEMA samples. The first three lower molecular weight PEMA samples gave curves with a common tangent that passes through $(\overline{M}_v)_r$ equals zero, while the experimental points for PEMA sample of the highest $\overline{M}_v$ value fell on a straight line which intersects the first at $(\overline{M}_v)_{rc}$.

The equations for the two straight lines are given as

$$(TS)_{max} = (TS)_1^* + L_1(\overline{M}_v)_r \tag{1}$$

and

$$(TS)_{max} = (TS)_2^* + L_2(\overline{M}_v)_r \tag{2}$$

where $(TS)_1^*$ and $(TS)_2^*$ are 4.0 and 3.7×10^4 N m^{-2} and L_1 and L_2 are 2.55 and 3.12×10^4 N m^{-2}, respectively. The straight line equation (2) was arrived at by the least square calculation.

The value of $(\overline{M}_v)_{rc}$ at the point of intersection of the two lines was calculated to be 4.91. It is evident that the two straight lines of Figure 6 could not possibly describe the same behavior and morphological variations in the blend, except at the point of intersection. The one represented by eq. (1) shows discontinuity and anomalous behavior. At $(\overline{M}_v)_r$ equals zero, the line indicates a $(TS)_{max}$ value of 4.0×10^4 N m^{-2} for a blend of PEMA

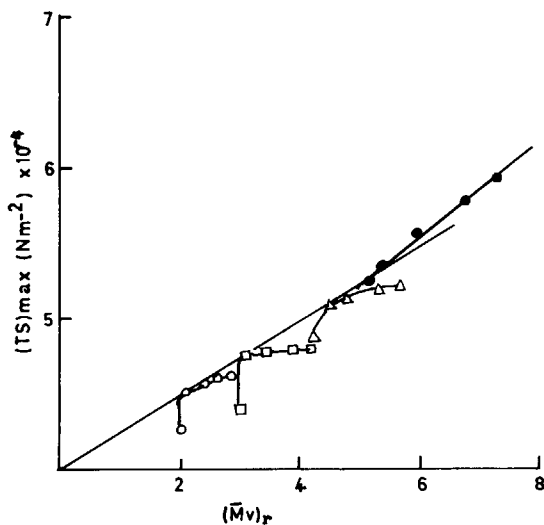Fig. 6.   Dependence of $(TS)_{max}$ of blend on $(\overline{M}_v)_r$ PEMA of $\overline{M}_v \times 10^6$: (○) 1.513; (□) 2.212; (△ 3.008; (●) 3.816 ($\times 10^6$).

of $\overline{M}_v$ approaching zero or a PVAc of infinitely large molecular weight value. This situation with eq. (1) appears to be highly theoretical, except at the points of tangent to the curves and intersection with the line of eq. (2). Prior to the point of intersection, the line of eq. (1) reveals a much larger improvement to TS of PVAc than anticipated, at least on the basis of eq. (2).

The line of eq. (2) thus describes a more practical situation. Homogeneous polymer mixtures and compatible blends of PVAc and PEMA might be assumed to be formed from $(\overline{M}_v)_r$ of about 4.9 with 18–20% PEMA producing the highest TS. The upper limit of $(\overline{M}_v)_r$ for formation of homogeneous mixtures and compatible blends of the polymers is not yet known. Our unconcluded study suggests that it might be as large as about 100.

Other portions of the curves for the three (PEMA) samples of lower molecular weight values suggest that the blends produced might experience phase separation to various extents. The closer the experimental points are to the tangent to the curves, the smaller the tendency to phase separation. Figure 7 confirms that $\Delta(TS)_{PVAc}$ at the peak of TS increased with $(\overline{M}_v)_r$. Also the four samples of PVAc of lower $\overline{M}_v$ values gave curves that intersect at $(\overline{M}_v)_r$ of about 4.9, while that for the PVAc sample of the highest $\overline{M}_v$ value remained widely separated from the others. Below $(\overline{M}_v)_r \approx 4.9$, lower $\overline{M}_v$, PVAc samples blend with PEMA to give the largest $\Delta(TS)_{PVAc}$ value. The reverse is observed for $(\overline{M}_v)_r > 4.9$. These results suggest that while it is insufficient just to keep $(\overline{M}_v)_r$ above about 4.9, the method of accomplishing this is also very important. It is better to keep $\overline{M}_v > 4.9$ by blending PVAc samples of sufficiently high molecular weight with PEMA samples of appropriately large molecular weight rather than work with PVAc sam-
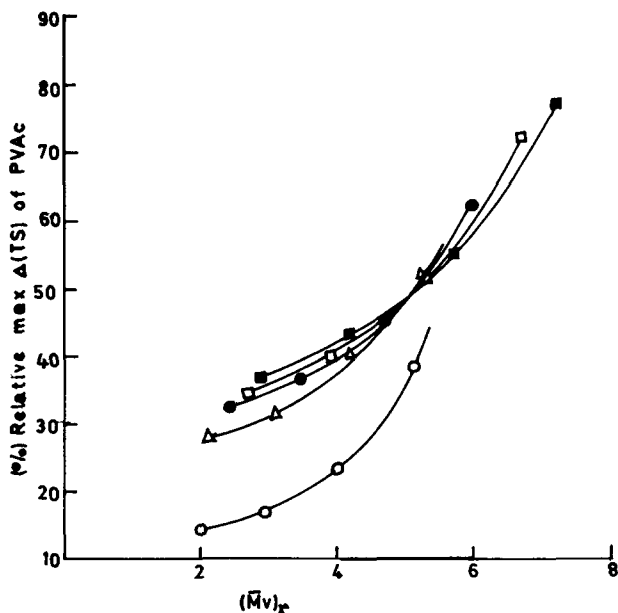

Fig. 7. The dependence of the % relative maximum change in TS of PVAc on $(\overline{M}_v)_r$ for PVAc of $\overline{M}_v \times 10^6$: (■) 0.531; (□) 0.570; (●) 0.638; (△) 0.721; (○) 0.745.

ples of very low molecular weight in order to optimize $(\overline{M}_v)_r$. Apparently, and on the basis of the fact that $(\overline{M}_v)_r$ should be equal to or exceed 4.9, the best results would be achieved with PVAc of $\overline{M}_v$ of 0.70–0.75 $\times$ 10^6.

At $(\overline{M}_v)_r$ of about 4.9, the percent relative maximum increase in TS of PVAc is about 50%. Thus the presence of PEMA in PVAc to the level of 20/80 (w/w) makes the TS of PVAc almost equal to that of the composite PEMA at $(\overline{M}_v)_r$ equals 4.9, and much higher than this value at $(\overline{M}_v)_r$ much greater than 4.9, from the results in Figures 2 and 7.

Figure 8 shows the variation of IM with blend composition. Initial modulus increased from its value for pure PVAc to a peak, then to a minimum, and finally towards the value for pure PEMA. The results for the PVAc samples of higher molecular weight values are not shown but have been used in arriving at subsequent figures. They show striking similarities to those of Figure 8, with differences in some details which are discussed in this paper. Similar to Figure 2 for TS, the additivity line might intersect the curve. Essentially for the four PEMA samples employed (curves for only three are shown), no area is below the additivity line. Generally (IM)$_{max}$ is obtained at about 20% PEMA in the blends, while (IM)$_{min}$ shifts to higher % PEMA values with increase in $(\overline{M}_v)_r$.

The peak IM values, plotted against $(\overline{M}_v)_r$, gave a family of curves similar to those of Figure 6. The common curve that touches the three separate ones for the PEMA of lower molecular weights and passes through $(\overline{M}_v)_r$ equals zero is parabolic. The experimental points on the fourth curve do not describe a straight line. This separate curve appeared to take off close to $(\overline{M}_v)_r$ of about 4.90 and touches the parabola near this value of $(\overline{M}_v)_r$. The dependence of (IM)$_{max}$ on the $\overline{M}_v$ of (PEMA) is similar to that in Figure 3 for (TS)$_{max}$. Generally (IM)$_{max}$ increased with $\overline{M}_v$ of PEMA as anticipated.
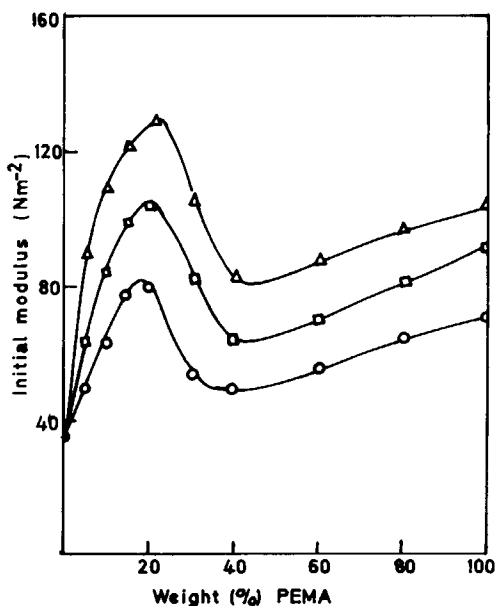

Fig. 8. Variation of IM with blend composition for PVAc of $\overline{M}_v$ equals 0.570 $\times$ 10^6 and PEMA of $(\overline{M}_v) \times$ 10^6 of: (◯) 1.513; (□) 3.008; (△) 3.816.

The variation of % elongation of films of the polymer blends with composition is represented in Figure 9 for only three out of the four PEMA samples, each blended with sample (S_2) of PVAc. The results for the other four PVAc samples are omitted, but follow the pattern described in Figure 9. Each curve shows a peak in % elongation at about 20% PEMA, then a sharp fall before finally and gradually approaching the value for PEMA. The additivity line cuts each curve. The smaller the molecular weight of the (PEMA) sample used in the blend, the larger the area of the curve above the additivity line. This is expected on the basis of the observations on TS and IM of the blends.

Figure 10 indicates that the peak value obtained for % elongation of the blends decreased with increase in $\overline{M}_v$ of the PEMA blended. It also had the highest value for the PVAc of the lowest molecular weight blended with PEMA of the lowest molecular weight.

The results represented in Figures 1–10, and others not presented here but which have been described, respectively in most cases, as similar to those presented, clearly indicate that PVAc, when blended with PEMA, produces results which can be significantly superior in mechanical properties to the parent polymers as reported by Lindsay et al.[4] for other systems. Generally when the two polymers are solution-blended in chloroform as the common solvent and cast into films as here described, they show good compatibility and miscibility over a wide range of composition, always up to about 30% PEMA. Usually a composition close to 20% PEMA gives an optimum improvement to the characteristics of either polymer.

Miscibility and compatibility of the two polymers as used here, respectively, mean their ability to mix on a macromolecular level and remain unmixed, and the formation of specific favorable interactions with themselves, leading to an improved molecular packing and often involving segmental and other conformational motions. This is in agreement with the reasonings of Olayemi et al.[10] and Shur and Ranby[11] on some other polymer
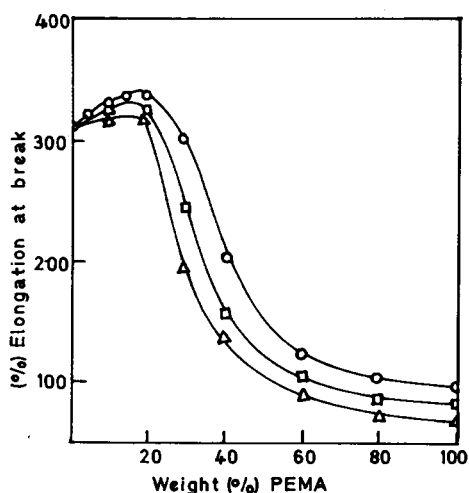

Fig. 9. Dependence of % elongation at break on blend composition for PVAc of $\overline{M}_v$ equals 0.570×10^6 and PEMA of $\overline{M}_v \times 10^6$ of: (○) 1.513; (□) 3.008; (△) 3.816.
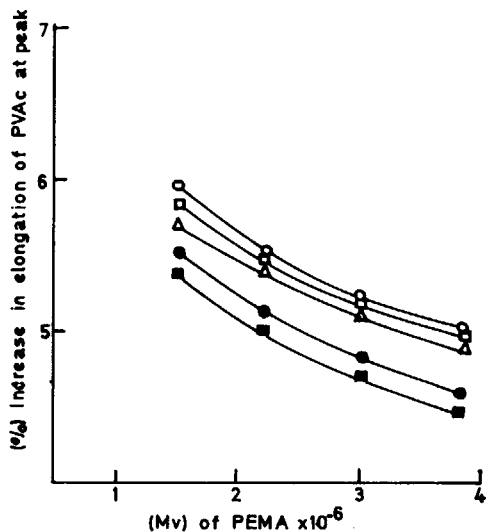
Fig. 10.   Dependence of peak value of % elongation at break on $\overline{M}_v$ of PEMA for PVAc of $\overline{M}_v \times 10^6$ of: (○) 0.531; (□) 0.570; (△) 0.638; (●) 0.721; (■) 0.745.

blends. Our definition of compatibility for the two polymers differs from that of Kuleznev and Mulnikova,[12] who expect a linear graph in the property–composition plot for partially compatible polymers. The type of interaction between two different polymers anticipated here should be possible mainly on account of the similarities in the monomeric structures, which in the case of PVAc and PEMA include the polar behavior. Other physicochemical characteristics of PVAc and PEMA, namely, their partial specific volumes and solubility parameters, which are fairly close[13] also indicate essentially similar behavior toward a common solvent and possibly toward themselves. These are additional strong supports for our claim of their compatibility at the molecular level.

Thus one very distinct type of blend is produced between PVAc and PEMA, with 80/20 (w/w) percent of the polymers. When the blend is formed in its solution in chloroform, alterations to its composition of 80/20 (w/w) of PVAc/PEMA leads to a reduction in the measured mechanical properties of the film obtained. It is reasonable to argue, therefore, that a homogeneous single-phase blend is formed as PEMA is mixed in chloroform with PVAc to the 20/80 (w/w) percent of PEMA/PVAc, but, thereafter, this blend could be assumed to be dispersed in PEMA on increasing the percentage of the latter in the system. The extent of dispersion should reflect the level of phase separation in the system. Phase separation is expected to increase as the extent of dispersion is decreased. Phase separation would also be affected by the efficiency of mixing during solution blending and that of solvent evaporation during film deposition on the mercury surface.

Any point on the property–composition curve below the additivity line is regarded to represent property except % elongation, obtained for blends with some phase separation characteristics, and the farther below the line, the greater the extent of phase separation in the blend. The chances of phase separation therefore increase as $(\overline{M}_v)_r$ of the blend system decreases.

Films of the blends with less than about 25% PEMA were all transparent, while tendency to opaque appearance increased as % PEMA increased and became maximum whenever a minimum occured in the property–composition plot. Further increase in the % PEMA towards 100 gave blends that were again transparent.

Thus two major types of blends appeared to have been formed, viz., one in which PEMA was dispersed in PVAc and the other with PVAc dispersed in PEMA as a medium. Certainly the bigger the sizes of the particles constituting the dispersion medium, the less the efficiency of the dispersion phenomenon. Thus large $(\overline{M}_v)_r$ values favour good dispersion of PEMA in PVAc. This improves entanglement or the chances of formation of a network structure,[14] maximizes (PEMA–PVAc) intermolecular interactions, discourages aggregation, and produces blends of uniform characteristics. The other type of blends where PVAc is dispersed in PEMA would not be expected to be very strongly dependent on $(\overline{M}_v)_r$ in this study as the molecular weights of all the PEMA samples are much bigger than those of the PVAc samples. It would require the matching of high molecular weight PVAc samples against very low molecular weight PEMA samples in order to be able to evaluate the dependence of the dispersion phenomenon on $(\overline{M}_v)_r$ for this type of blends. It is, however, very unlikely on the basis of the results reported here, and from the arguments of Dobry and Boyer-Kawenoki[15] and Paul,[16] that two polymers with equally large molecular weights would be compatible.

Molecular weight distribution effects on blending of PEMA with PVAc have not been evaluated. Essentially there would be some effect on the peak values of TS, IM, and % elongation at break of the films from the polymer blends. From the present study it is evident that an average value of each property should be expected for polymer samples of broad molecular weight distribution.[17,18]

Some consequencies of the strong interaction between PVAc and PEMA reported here are very important, particularly in the technology of the polymers and their blends. The rheological aspect has been mentioned in our previous paper.[19] The stability of the blends of the two polymers to thermal, UV and other radiation treatments, the tolerance of conventional plasticizers, gas permeability, etc. are properties of technological interest in PVAc/PEMA blends. Some of these areas are presently receiving attention in this laboratory.

CONCLUSIONS

From the present study, it is concluded that PVAc forms compatible blends with PEMA over a wide range of wt% of PEMA. Strong intermolecular interactions of the PVAc–PEMA type are mainly involved.

Twenty percent PEMA produces the optimum effect on TS, IM, and % elongation at break of the films obtained from the blends.

Films from blends with up to 30% PEMA, and, in particular, those with 20% PEMA, have high values of TS, IM, and % elongation at break, and are, on the basis of the mechanical properties studied, significantly superior to the individual polymers that constitute the blends.

The improvement made to the properties of the separate polymers due to blending are critically dependent on the ratio of the viscosity average molecular weight values $(\overline{M}_v)_r$ for the system.

The smallest $(\overline{M}_v)_r$ value, i.e., $(\overline{M}_v)_{rc}$, recommended for blends exhibiting no phase separation and of excellent mechanical properties with 20% PEMA is 4.9. An upper value of $(\overline{M}_v)_r$ is tentatively estimated to be of the order of 100.

There is tendency for phase separation in the system with PVAc samples of very high molecular weight values for which the $(\overline{M}_v)_r$ values are smaller than $(\overline{M}_v)_{rc}$.

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