

Compatibility Studies on Blends of Poly(ethylene Ortho-phthalate) and Poly(vinyl Acetate)

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Synopsis

Blends of poly(ethylene ortho-phthalate) (PEOP), and poly(vinyl acetate) (PVAc), appear to be compatible at all compositions, from visual examination at room temperature and differential scanning calorimetry tests. Both low- (PEOP-1) and high-molecular weight (PEOP-2) alloys with PVAc show a single composition-dependent glass transition temperature (T_g). Some blends show T_g values that are below the T_g for either of the pure polymers. Couchman's equation, with a slight modification, can be used to model T_g behavior. All PEOP-2 blends with PVAc, phase separate at high temperatures, whereas PEOP-1-PVAc blends remain miscible under the same conditions. The composition dependence of the blends refractive index shows a deviation from simple additivity rules, and a similar trend is observed in density measurements. When comparing Flory's characteristic parameters for the polymers, compatibility is predicted for PVAc-PEOP blends. In contrast, blends of PEOP and poly(methyl methacrylate) (PMMA), which has a similar chemical structure to that of PVAc are predicted to be incompatible, in agreement with experimental evidence. It is suggested that compatibility is produced because of possible specific interactions between the aromatic group of PEOP and the ester carbonyl on PVAc, which is not sterically hindered as is the corresponding moiety on PMMA.

INTRODUCTION

The search for compatible polymer alloys continues to be one of the most important activities within the field of polymer blends. Undoubtedly, one of the main attractions in this area is the potential accessibility to a wide variety of properties which can be tailored from the simple physical combination of two compatible polymeric components.¹

From the standpoint of finding miscible polymer pairs, devising and testing screening procedures for the *a priori* selection of the polymers to be matched is a highly important objective. Several studies in this direction have been pursued from a theoretical viewpoint by Sanchez and co-workers,^{2,3} Flory, Simha, and others.^{4,5} In a more practical approach by Paul and co-workers^{6,7} the state of miscibility of two given polymers is compared with the sign of the heat of mixing of their low-molecular weight analogs. It has been found that an exothermic heat of mixing of the analogs usually implies a high degree of compatibility between the polymers.⁹

Following this line of thought, reports in the literature,⁸⁻¹¹ show that the presence of a carbonyl moiety on one polymer, coupled with the presence of a phenyl ring on the other is a favorable situation for compatibility.⁹ Thus, the prediction of likely candidates to form compatible polymer alloys

could be ideally reduced to the search of low-molecular weight compounds whose binary liquid mixtures show exothermic behavior.

We set out to investigate the possibility of finding a polymeric plasticizer for poly(vinyl acetate), PVAc, in order to increase its range of application, keeping in mind the above carbonyl-aromatic ring interaction. Poly(ethylene-ortho-phthalate), which meets the stated conditions, was tested and found to effectively plasticize PVAc, forming a compatible polymer system, whose detailed study is presented here.

EXPERIMENTAL

Preparation of Poly(ethylene Ortho-Phthalate) (PEOP)

A mixture of phthalic anhydride (1 mole), ethylene glycol (1.15 mole), and trihydrated sodium acetate (0.05 mole) was heated in a beaker to boiling while continuously stirring until the reaction mass became a viscous liquid (1 hour). Then, the mixture was allowed to cool and dissolved in three volumes of chloroform; a small portion of ethanol was added (2% by volume of mixture) and the mixture washed with one volume of water for every 5 volumes of raw polymer in a separation funnel. The washed solution was cooled in an ice bath and poured into a comparable volume of cool diethyl ether. The resulting precipitate was recovered by decanting, and allowed to stand at 70°C and reduced pressure for 20 hours.

A portion of the PEOP obtained as described above was heated at 150°C under reduced pressure for 5 hours, in order to carry the reaction a step further to completion, thus producing a polymer with a higher molecular weight. In this paper, the latter is referred to as PEOP-2 to distinguish it from that of lower molecular weight (PEOP-1).

Infrared spectra of PEOP-1, PEOP-2, and PVAc, were obtained with an IR Perkin Elmer 683 Spectrophotometer to assess the chemical structure of each polymer, under standard operating conditions, between 400 and 4000 cm^{-1} . Samples of the polymers were dissolved in chloroform and cast on a KBr window by allowing the solvent to evaporate at 50°C.

Characteristic IR bands for PEOP are as follows: C=O and C—O stretch vibrations (ester), 1720 and 1120 cm^{-1} ; aromatic ring vibrations, 1590 and 1560 cm^{-1} ; methylene vibrations, 1475 and 1440 (bending), and 1360 and 1330 (wagging).

Also, the molecular weights of PEOP-1, PEOP-2, and PVAc, were determined by gel permeation chromatography, using a Waters Associates GPC 200, fitted with Styragel columns with porosities of 10^4 and 10^5 Å, respectively, and a flow rate of 1 ml/min with tetrahydrofuran used as a solvent.

Preparation of PEOP-PVAc Blends

Blends of either PEOP-1 or PEOP-2 and PVAc were prepared by dissolving both components in chloroform, and then casting on a petri dish, subsequently allowing the solvent to evaporate at room temperature. The thin films obtained were maintained at 80°C under reduced pressure for 42 hours. Solvent-free films of the blends and each individual polymer were then tested as described below.

Blend Characterization

Differential scanning calorimetry tests were carried out in a DuPont-990 DSC apparatus. Three runs were performed for each specimen by duplicate, with a heating rate of 10°C/min; from -40 to 170°C and under a dynamic nitrogen atmosphere.

For phase separation studies, samples of the blends, and the single polymers, were placed in between two microscope thin cover glass slides and heated at 20°C/min, in a Fisher-Johns Melt-point instrument in order to detect, visually, any temperature-induced phase separation phenomenon.

Measurements of refractive indices, n_D^{25} , were carried out in an Abbé refractometer of Erma Optical Works, Ltd., in the following manner: the sample was dissolved in chloroform and some drops of this solution were deposited on circular microscope glass slides, evaporating the solvent at 100°C for 5 hours under reduced pressure, and adhered onto the refractometer's prism with 1-bromonaphthalene. The uncovered surface of the prism was covered with thin black paper. Finally, blend densities were determined with a pycnometer at 25°C, using water as the reference liquid.

Molecular Weights

The first sample of poly(ethylene ortho-phthalate) prepared in this work had a number average molecular weight of 5100, higher than that reported by Fischer¹² for a PEOP obtained from phthalic anhydride and ethylene oxide ($M_n=3325$); the molecular weight of PEOP-2 was indeed increased by heating at 150°C, as shown in Table I.

RESULTS AND DISCUSSION

Visual Observations

All blends obtained were either highly viscous liquids or tough solids at room temperature and appeared transparent to visual examination: hence, it was reasonable to suspect that the polymeric pair PEOP-PVAc was miscible in a wide composition range.

Thermal Analysis

DSC thermograms showed a single glass transition temperature (T_g), for each blend, as can be seen in the DSC curves, some of which are shown in Figure 1. Thus, from this observation, the PEOP-PVAc system can be considered as fully compatible, in principle.

TABLE I
Molecular Weights of PEOP and PVAc

Polymer	\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$
PEOP-1	5100	5700	1.11
PEOP-2	9500	29,900	3.14
PVAc	75,800	318,850	4.20

PVAc was obtained from the Hoechst Co. Its trademark is Mowillith-60.

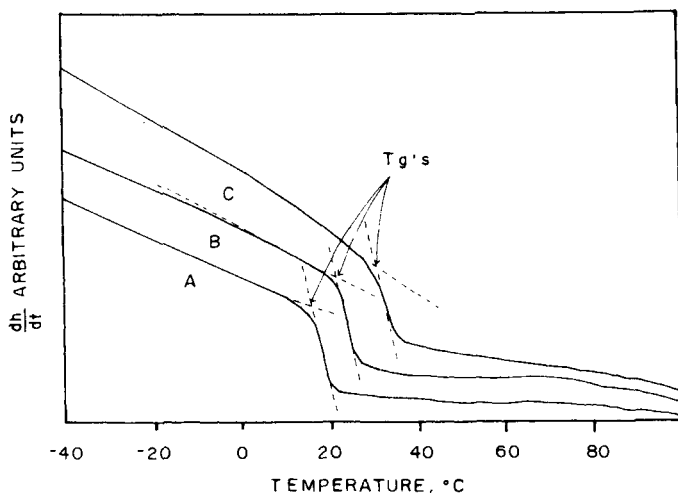


Fig. 1. Some typical DSC thermograms for PEOP/PVAc blends: A = 75%, B = 50%, and C = 25% of PEOP.

It is a well known fact that the experimental T_g 's of the blends have intermediate values between those of the single polymers; however, the composition dependence of T_g for this system, shown in Figure 2, presents a peculiar feature. Blends containing 85, 90, and 95% of PEOP, have T_g values up to 7°C lower than that of this polymer, even though the latter has the lower T_g of both pure polymers. Thus, PVAc appears to "plasticize" PEOP when first added in small amounts; but, as the blend becomes richer in the former, whose T_g is above that of PEOP, the glass transition temperature for the system tends toward the PVAc- T_g , and remains intermediate between those of the pure polymers, as happens in most miscible blends.

To address this unexpected situation, one must first take into consider-

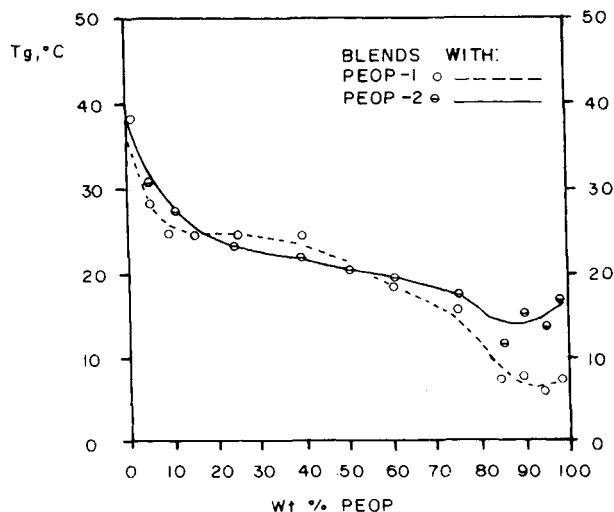


Fig. 2. Composition dependence of T_g for the PEOP/PVAc system.

ation that the T_g of polyesters is greatly influenced by their degree of crystallinity;¹³ in general the higher the crystallinity of the polymer, the higher its T_g . Thus, a disruption in the state of order of the polyester causes a depression in its T_g . This is a well documented fact for poly(ethylene terephthalate) (PET),¹⁴ and poly(ϵ -caprolactone) (PCL).¹⁵ Moreover, miscible blends of PCL and polyvinyl chloride (PVC), as reported by Koleske and Lundberg,¹⁵ show a behavior similar to what has been observed here. That is, even though the T_g for PVC is higher than that of PCL, the PCL T_g is depressed at low PVC contents. It has been further explained that this comes about because part of the PCL crystalline phase is disrupted.¹⁵

One cannot claim crystallinity nor crystallizability for PEOP in the bulk, because annealing of the pure polymer at different temperatures between 25 and 100°C does not produce any detectable crystallization.⁹ However, certain solvents can induce the appearance of a crystalline phase in PEOP.¹² Evidently, this is possible because PEOP possesses a highly regular backbone, although less planar than that of PET. Conix and Van Kerpel¹⁶ have explained the higher crystallizability of PET compared to that of PEIP in terms of planarity.

Thus, it is possible that at least short-range order exists in the bulk for PEOP, and PVAc might then be thought of as a means to produce a disruption in the short-range ordered regions in PEOP at low concentrations, similar to what is mentioned above for the PVC-PCL system. More detailed studies are necessary in order to verify this hypothesis.

An alternative way of looking at the problem is to study the composition dependence of T_g in terms of Couchman's approach.¹⁷

In this sense, T_g versus composition curves (Fig. 3) can be simulated by using the following equation:

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2} - Kw_1w_2}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (1)$$

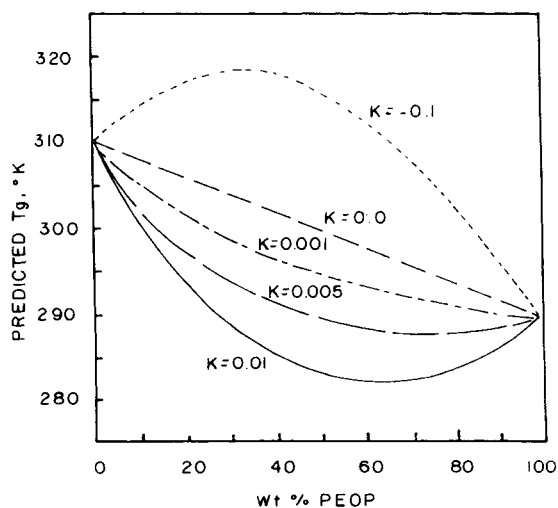


Fig. 3. Modeling the composition dependence of T_g for the PEOP/PVAc system, using a modified version of Couchman's equation.

This equation is identical to the one originally derived by Couchman, except for the Van Laar-type term (Kw_1w_2), that appears in our Eq. (1), as a result of the difference in excess extropies of mixing of the glassy and the liquid phase:

$$Kw_1w_2 = \Delta S_g^E - \Delta S_l^E \quad (2)$$

The parabolic dependence arbitrarily assigned to this term follows a similar simple form proposed by Prigogine and Defay.¹⁸ Couchman¹⁷ leaves this term out of his final expression because it appears to be relatively small. However, as can be observed on Figure 3, with K values as low as 10^{-3} , which implies that the whole term has an order of magnitude of about 10^{-4} , the observed behavior can be approximately simulated.

The exact physical meaning of this occurrence is not yet clear, since independent evaluations of each ΔS^E term are needed to venture a possible explanation; however, it seems to be important, at least for systems as the one shown here, to account for such a small contribution.

Phase Separation Induced by Temperature

All PEOP-2-PVAc blends separate into two phases (Fig. 4) when gradually heated from 25 to 240°C. The process was found to be reversible, that is, all blends became clear on cooling below the separation temperature, but turned opaque when reheated above their cloud point. The phenomenon was not observed to occur in low-molecular weight or PEOP-1 blends with PVAc.

These observations, characteristic of lower critical solution temperature

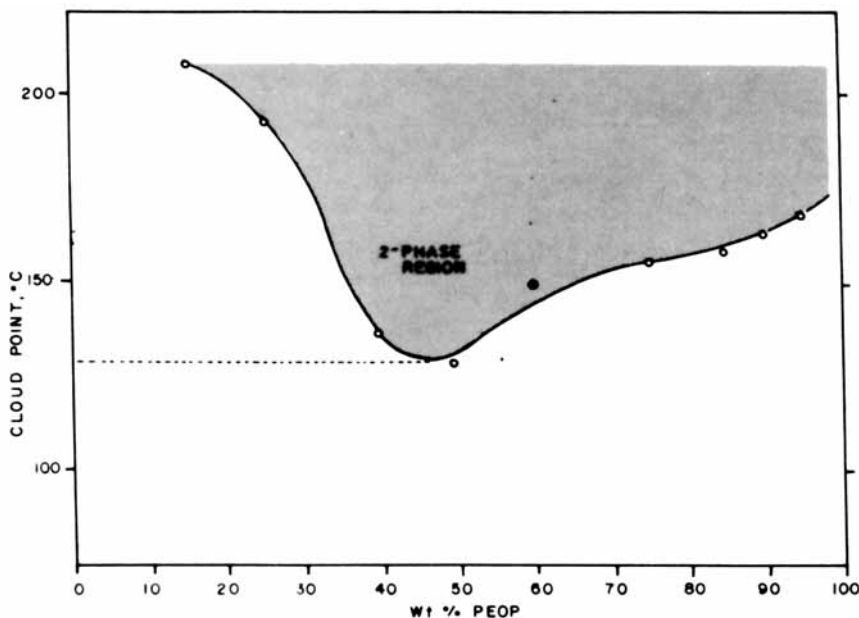


Fig. 4. Cloud point curve for PEOP-2/PVAc blends.

(LCST) behavior, are in line with earlier theoretical investigations by McMaster,¹⁹ and other experimental evidence for binary polymeric systems.²⁰⁻²² Apparently, the LCST becomes higher as the molecular weight is lowered, up to a point where the minimum phase separation temperature is above the ceiling or degradation point for any of the polymers and, hence, cannot be observed any more.

The asymmetric nature of the phase-separation curve, on Figure 4, has been reported for other miscible polymeric systems.^{21,22} Such an effect has been correlated with the molecular weight difference between both polymers,¹⁹ and, although the thermal expansion and thermal pressure coefficient can also influence this behavior,¹⁹ it is clear that the phase-separation curve is tilted toward the region where the blends are richer in the lower molecular weight polymer,¹⁹ as is the case for the PEOP-PVAc blend.

Refractive Index

The variation of the refractive index, n , with composition, for the blends, shows a deviation from simple additivity, as seen on Figure 5. The large deviation observed is probably influenced by the changing T_g of the system, and the position of the latter with respect to room temperature. As indicated in the Figure 5, the onset of large deviations occurs when T_g for the system

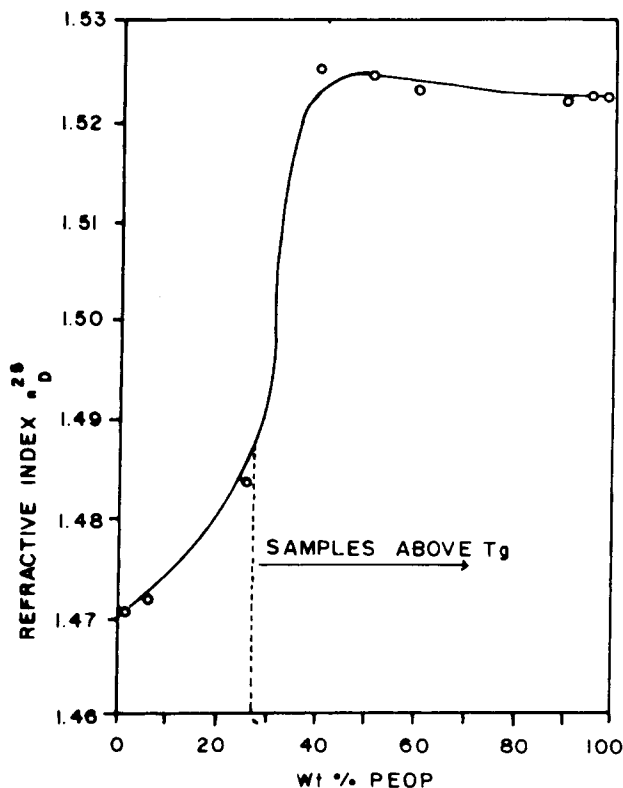


Fig. 5. Composition dependence of the refractive index, n_D^{20} , for the PEOP/PVAc system.

is approximately ambient temperature. Thus, below this T_g value, one is testing a glassy polymeric system, with a lower refractive index than that of similar compositions that are in the rubbery state.

One might also add, at this point, that density measurements appeared to have a similar trend for the system, that is, the blends show densities higher than those predicted from simple additivity. In addition to the glassy to rubbery transition brought about by composition variation, swelling of either one of the polymers by the liquids used appeared to obscure the results, with water being the most appropriate medium, but also with an uncertain swelling role.

Equation of State and Other Related Considerations

With the purpose of finding further explanation to the outcome of our results, we tried out the concept of specifically interacting moieties on one more polymer pair. Thus, studies carried out separately on mixtures of PEOP with poly(methyl metacrylate) show that, at most, these two polymers are semicompatible. This is somewhat unexpected, since the chemical structures of PMMA and PVAc are fairly similar. In order to analyze this occurrence and, at the same time, to deepen our understanding for the PVAc-PEOP system, we followed two routes: one was to examine the equation of state parameters of PMMA, PVAc, and PEOP; the other, was to inspect models of the respective chemical structures, and to pinpoint the possible features that affect miscibility.

Drawing conclusions about the compatibility of two polymers from statistical thermodynamical methods such as Flory's new equation of state⁴ is a highly complex task requiring both sophisticated calculations¹⁹ and accurate experimental information, which sometimes is incomplete or totally unavailable.²³ However, Somani and Shaw²³ have used a simplified approach, which allows a rapid, although approximate, evaluation of compatibility in a polymer system, based only on the rules and characteristic parameters of the above theory. The latter characteristic pressures, temperature, and volume in Flory's model are defined, respectively, as:⁴

$$P^* = \tilde{v}^2 T \alpha / \beta \quad (3)$$

$$T^* = T \tilde{v}^{4/3} / (\tilde{v}^{1/3} - 1) \quad (4)$$

$$v_{sp}^* = v_{sp} \left[\frac{1 + T\alpha}{1 + 4T\alpha/3} \right]^3 \quad (5)$$

Where v_{sp} , specific volume, is related to the mass density of the component, ρ , $v_{sp} = 1/\rho$; $\alpha = \delta \ln V / \delta T]_p$ is the thermal expansion coefficient, and $\beta = -\delta \ln V / \delta p]_T$ is the isothermal compressibility; $\tilde{v} = v_{sp} / v_{sp}^*$ is the reduced volume, and T is temperature in degrees Kelvin. Equations (3) to (5), combined with a knowledge of the values of $v_{sp}(T)$, $\alpha(T)$, and $\beta(T)$, are sufficient for the determination of v_{sp}^* , P^* , and T^* . Thus, as pointed out by Somani and Shaw, Flory's equation of state requires, for compatibility between two polymers: (i) If the characteristic temperatures for the poly-

mers are such that $T_1^* > T_2^*$, the relation between the corresponding characteristic pressures must be $P_1^* > P_2^*$, and (ii) the absolute value of the difference between T_1^* and T_2^* must not exceed 200°K.

The calculations needed to evaluate the above parameters, are defined in the literature.^{4,23} Individual specific volumes were calculated using the Simha-Boyer model as described by Van Krevelen;²⁴ the isothermal compressibility coefficients were assumed to be temperature dependent and obtained from the derivative of the Tait equation with respect to pressure²⁴ at constant temperature; the temperature-dependent constant for PEOP, which appears in this equation, was estimated following a group contribution method.²⁴ All calculations and assumptions are detailed elsewhere.²⁵

It is important to remark that Flory's model is applicable, as a theory for fluid mixtures, above the glass transition temperature. Also, the decomposition temperature for each polymer is an upper practical limit.

Figure 6 shows the values for T^* and p^* obtained for each individual component as a function of temperature. Based on these results, one can

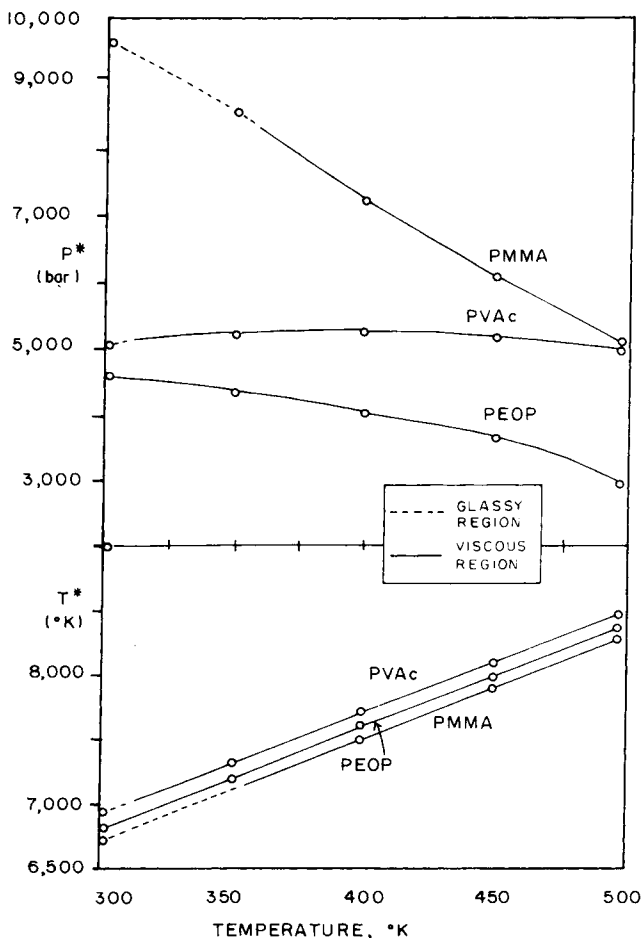


Fig. 6. Flory's characteristic pressure, p^* , and temperature, T^* , values for PEOP, PVAc, and PMMA, calculated from Eqs. (3) to (5).

detect that PEOP and PVAc meet the stated conditions for miscibility. On the other hand, the required parameter ratios are not fulfilled by the respective T^* 's and p^* 's for PEOP and PMMA. Thus, incompatible systems should come out of these mixtures, which is in agreement with our experiments. Nevertheless, the miscibility of PEOP and PMMA apparently increases with temperature.

Therefore, Flory's equation of state qualitatively predicts the miscibility characteristics found experimentally for the mixtures. It is evident that these results are only approximate but, at the same time, show that it seems feasible to make an *a priori* qualitative assessment of compatibility, following the simple method used by Somani and Shaw.

From an alternative standpoint, when considering molecular models of the chemical moieties involved as represented in Figure 7, further explanations for the above behavior can be inferred. It has been observed that carbonyl-containing low molecular-weight compounds, such as ketones and esters, show exothermic behavior when mixed with a number of phenyl or phenylene derivatives, similar to the PEOP repeat unit.²⁶ Hence, a specific interaction between the carbonyl group of one polymer, and the phenylene ring of the other, has been suggested to be a determinant factor for compatibility in a number of polymers.¹⁰

Although both PVAc and PMMA have carbonyl groups, it is apparent that the possible positive inductive effect from the methyl group forming

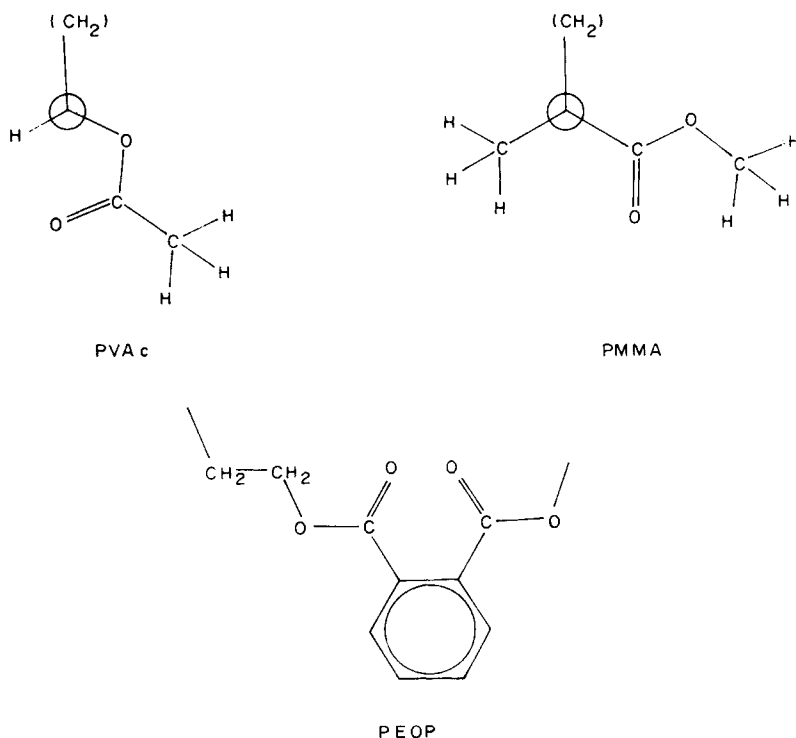


Fig. 7. Chemical structure of the repetitive units for poly(ethylene ortho-phthalate), poly(vinyl acetate), and poly(methyl methacrylate).

the ester in PMMA (Fig. 7) on the carbonyl group, that enriches its electron density, is weakened by the oxygen lying between the carbonyl and methyl. This is not the case with PVAc, where the methyl group is directly linked to the carbonyl moiety, making the latter more polar than that of PMMA. Interestingly, PMMA shows a dipole moment of 1.29–1.35 D (in benzene, at 30°C), while PVAc has a corresponding value of 1.61–1.70 (in benzene, at 25°C).²⁷

Besides the above argument, one can take into consideration that the methyl pendant group on the PMMA chain, instead of the hydrogen in the equivalent position for PVAc, could cause some degree of steric hindrance for the interaction of the PMMA carbonyl with the PEO aromatic ring. It is worthwhile to note that, apparently, the methyl on the acetate group of PVAc, is more separated from the carbonyl than is the corresponding group of PMMA (Fig. 7), contributing, in this form, to increase the above-mentioned steric hindrance effect.

CONCLUSIONS

Poly(ethylene ortho-phthalate) and poly(vinyl acetate) form compatible blends in the whole composition range, as seen from thermal analysis results, which indicate that there is a single and composition-dependent glass transition temperature for the system when using two different molecular weight levels of PEO. Blend clarity is also observed in all specimens at room temperature, which supports the above conclusion. Optical measurements show, nonetheless, that the refractive indices of the blends are higher than the arithmetic average values of the components.

Temperature-induced phase separation was detected for the blends that contain the higher molecular weight PEO, while the ones containing the PEO of lower degree of polymerization are apparently miscible at all temperatures. This is in agreement with theoretical predictions and experimental findings for other systems.^{8,19,20,22}

In terms of Flory's equation of state, PEO and PVAc are miscible because they fulfill the requirements of characteristic parameter ratios, as suggested by Somani and Shaw.²³ In contrast, PMMA, which has a similar chemical structure to that of PVAc does not form compatible blends with PEO, as verified experimentally, because it does not fit the minimum equation of state conditions necessary for miscibility.

The presence of a carbonyl group in PVAc, free of steric hindrances and with a higher polarity in comparison with that of PMMA, appears to be the relevant cause for miscibility through a specific interaction with the PEO phenylene moiety, as reported for other polymers.¹⁰

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