Polymer–polymer miscibility prediction from polymer (1) analogue probe–polymer (2) exchange interaction parameter using inverse gas chromatography: the miscibility of poly(vinyl methyl ether) with poly(vinyl ester)s

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The polymer (1) analogue probe–polymer (2) exchange interaction parameter (X_{12}) as determined by inverse gas chromatography (i.g.c.) has been used to predict the miscibility in poly(vinyl ester)s (1) and poly(vinyl methyl ether) (PVME) (2) blends. The hydrogenated monomers of the poly(vinyl ester)s have been used as the analogue probes and PVME as the stationary phase in i.g.c. A miscible system is predicted when X_{12} has a negative value. The prediction agrees well with the experimental miscibility results based on film clarity and glass transition temperature measurements. This study establishes that PVME is miscible with poly(vinyl propionate) and poly(vinyl butyrate) but immiscible with poly(vinyl acetate).

(Keywords: miscibility; PVME; poly(vinyl ester)s; exchange interaction parameter; polymer analogue probe; T_g)

INTRODUCTION

Miscible binary polymer blends generally result when the component polymers interact specifically with each other leading to exothermic heat of mixing. In order to predict polymer–polymer miscibility, therefore, one has to anticipate whether the mixing is exothermic or endothermic. According to the modern solution theories the heat of mixing arises from two effects: (i) the exchange interaction and (ii) the free-volume differences between the components of the mixture $(\Delta V_f)^{1-6}$. The latter leads to an evolution of heat which is large when ΔV_f is large, as in polymer–solvent systems. For polymer–polymer as well as solvent–solvent systems the contribution of ΔV_f to ΔH_m is small. ΔH_m in these systems therefore represents predominantly the exchange interaction energy. Paul *et al.*[7] proposed that the heats of mixing of low-molecular-weight polymer analogous compounds called polymer analogues may approximate the heats of mixing of the polymers. They showed for blends of polycarbonates and polyesters that miscibility in these systems is consistent with the heat of mixing of the polymer analogues[7]. The analogue calorimetry has since been used to determine the heat of mixing in polymer blend systems[8–12].

On the other hand, from i.g.c. studies the exchange interaction energy between small-molecule probes and polymer segments may be derived[13–17]. In fact, a vast i.g.c. literature exists which gives the values of the exchange interaction parameter X_{12}, as defined in the Prigogine–Flory theory, for a great many probes (1) and polymers (2). Some of the probes may be good polymer analogues. The $X_{12} < 0$ cases may be used to design new miscible polymer blends (2 + 3) where the probe (1) is an analogue of polymer (3) and (2) refers to the polymer used as the stationary phase in the i.g.c. work. In earlier i.g.c. work from this laboratory it has been shown that hydrogenated monomers can be good polymer analogues[18,19]. Klotz *et al.*[20] also used a hydrogenated monomer, i.e. ethyl benzene, as an analogue for polystyrene in their i.g.c. study of the thermodynamics of interaction between polystyrene (PS) and poly(vinyl methyl ether) (PVME). The latter was used as the stationary phase and ethyl benzene the probe. In their work the exchange interaction energy parameter X_{12} turned out to be negative. This result supported the view that PS and PVME interact specifically.

In this paper we report on our search for new polymer blends on the above lines using the X_{12} data from i.g.c. literature and also our own X_{12} data for the hydrogenated monomer probes. Thus, from the work of Klotz *et al.*[20] we find that the exchange interaction energy for ethyl acetate probe and PVME segments is exothermic. Since ethyl acetate is the hydrogenated monomer of poly(vinyl acetate) (PVAc) we expect that PVME and PVAc would be miscible, although from the functional groups present in these two polymers (ether and ester) one would hardly expect any specific interaction between them. However, our expectation was emboldened from the work of Kalfoglou *et al.*[21,22] who reported that poly(ethylene

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oxide) (PEO) (ether functional group) is miscible with PVAc (ester functional group). Also, PEO is reported to be miscible with poly(methyl methacrylate)[23,24] and PVME with some polyacrylates[25].

In this work, apart from checking the miscibility of PVME with PVAc we have examined also the miscibility of the former with other poly(vinyl ester)s, namely poly(vinyl propionate) (PVPr) and poly(vinyl butyrate) (PVBu), and determined the thermodynamic interaction parameters by i.g.c. using the hydrogenated monomers of the poly(vinyl ester)s as the probes (1) and PVME (2) as the stationary phase. The prediction of miscibility based on the i.g.c.-determined interaction parameters was then tested with the miscibility studied from film clarity tests and glass transition temperature measurements. A preliminary report on this subject was published earlier by us[26].

EXPERIMENTAL

PVME ($\bar{M}_v = 5.2 \times 10^4$) was an Aldrich product supplied as a 50 wt% solution in water. On warming the solution the polymer separated out; it was then dried in a vacuum oven at 90°C for 72 h. The following poly(vinyl ester)s were used: a low-molecular-weight and a medium-molecular-weight PVAc, PVAc (l) ($\bar{M}_v = 27\,960$) and PVAc (m) ($\bar{M}_n = 69\,500$, $\bar{M}_v = 160\,500$); PVPr ($\bar{M}_n = 47\,000$, $\bar{M}_v = 62\,650$); and PVBu ($\bar{M}_n = 111\,650$, $\bar{M}_v = 146\,470$). The polymers were prepared in the laboratory by the solution polymerization technique using ethyl acetate solvent and 2,2′-azobisisobutyronitrile (AIBN, 0.06% w/v) initiator at 60°C. The monomers vinyl acetate and vinyl butyrate were commercial products while vinyl propionate was prepared in the laboratory following Adelman's method[27]. The monomers were freed from inhibitors, distilled and used. The $\bar{M}_n$ values were determined osmometrically using benzene as a solvent with the help of an hp 501 high speed membrane osmometer and Schleicher & Schuell RC 51 membranes. The $\bar{M}_v$ values were determined viscometrically in benzene at 30°C using the Mark–Houwink equation

$$[\eta] = K\bar{M}_v^{\alpha}$$

for which the values of K and α were obtained from the literature[28]. The polymer blends were prepared by mixing 2% (w/v) solutions of the polymers in appropriate proportions in benzene or acetone and casting films. The blends were dried for 72 h in a vacuum oven at temperatures which were at least 50°C higher than the glass transition temperatures (T_g).

The T_g values were determined using a Perkin–Elmer DSC-2 differential scanning calorimeter calibrated with indium. The blends were annealed at 80°C in the apparatus for 15 min and then quenched to −50°C where they were held for 10 min. The samples were then scanned at a heating rate of 10°C min^{-1}. T_g values were taken as the onset of the change of slope in the heat capacity plot.

Inverse gas chromatography

The procedure described by Bhattacharyya *et al.*[18,19] was followed. PVME was loaded onto a chromosorb support (Supelco, 60/80 mesh, acid washed, dichlorodimethylsilane treated) from solutions in benzene. The coated support was dried in vacuum at 100°C for 3 days. The percentage loading (7.54) was determined by the calcination method (following Vogel[29]) with the usual blank correction[30]. The weight of PVME in the column was estimated to be 0.7907 g.

The specific retention volume V_g^0 (cm^3 g^{-1}) values for the probes randomly varied, although to only a small extent, with the flow rates. So, the average value of V_g^0 obtained at different flow rates was used. The standard deviation in V_g^0 at the highest temperature used (120°C) was within 1–2%; at lower temperatures the standard deviation was within 2–3%.

Data reduction

The polymer–probe interaction parameters χ_{12} were calculated using[31]

$$\chi_{12} = \ln\left(\frac{273.15Rv_{2,\mathrm{sp}}}{P_1^0 V_{g2}^0 V_1}\right) - \frac{P_1^0(B_{11} - V_1)}{RT} - \left(1 - \frac{V_1}{V_2}\right) \quad (1)$$

where subscript 1 refers to the probe and 2 refers to the polymer stationary phase (PVME in this case). V_1 and V_2 are the molar volumes of the probe and polymer, respectively, at the column temperature (T). P_1^0 and B_{11} are the vapour pressure and the second virial coefficient, respectively, of the probe at the column temperature and R is the gas constant. The densities of the solvents and P_1^0 at the column temperature were obtained from the literature[32–34]. B_{11} values were calculated using the McGlashan and Potter[35] equation

$$B_{11}/V_c = 0.43 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (2)$$

where V_c and T_c are the critical molar volume and the critical temperature of the solute, respectively, and n is the number of carbon atoms in the alkanes or the number of corresponding groups in the non-alkane solutes. The non-combinatorial free energy of the mixing parameter χ_{12} as calculated from equation (1) is based on the Flory–Huggins theory of polymer solution thermodynamics. However, for the application of the Prigogine–Flory theory the appropriate value of the parameter is obtained by replacing the specific volume terms in equation (1) with core specific volumes (specific volume at 0 K), and the parameter thus determined is identified as the starred quantity χ_{12}^*. The exchange interaction parameter X_{12}, as defined by the Prigogine–Flory theory, was calculated from a knowledge of χ_{12}^* and the characteristic parameters for pressure P^*, volume V^* and temperature T^* of the components by using equation (3) (following Patterson and Delmas[5,6])

$$RT\chi_{12}^* = \frac{V_1^* X_{12}}{\tilde{V}_2} + P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} + 3\tilde{T}_1 \ln\left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1}\right)\right] \quad (3)$$

where the first term on the right-hand side of equation (3) is the interactional term and the second term is the free-volume term and

$$\tilde{V} = V/V^* \quad (4)$$

$$\tilde{T} = T/T^* = (\tilde{V}^{1/3} - 1)\tilde{V}^{-4/3} \quad (5)$$

$$\tilde{V}^{1/3} = 1 + \frac{\alpha T}{3(1 + \alpha T)} \quad (6)$$

The calculation of the X_{12} parameters using the above equations was done using an iterative procedure following the method of Su[36], an outline of which is given by Mandal *et al.*[14]. The values of the characteristic parameters and their sources are given in *Table 1*.

RESULTS AND DISCUSSION

Film clarity and T_g *studies*

Films cast from benzene and acetone for the PVME–PVAc blends over the whole range of compositions were opaque even for the low-molecular-weight PVAc sample. On the other hand, films of PVME–PVPr and PVME–PVBu blends were clear at all blend compositions. These results gave the first indication that PVME is immiscible with the first member of the poly(vinyl ester) family, namely PVAc, but miscible with the next two higher homologues, namely PVPr and PVBu. These inferences found further support from the T_g studies. The differential scanning calorimetry (d.s.c.) traces for all three blend systems at various blend compositions are shown in *Figures 1* to *3*. It is clear from the figures that the blends of PVME and the low-molecular-weight PVAc, namely PVAC (1), exhibit two T_g values which are close to those of the pure components, while the PVME–PVPr and PVME–PVBu blend systems both exhibit a single T_g.

The T_g–composition diagrams for the PVME–PVPr and PVME–PVBu blend systems are shown in *Figures 4* and *5*, respectively. The curves lie below the lines representing the weight-average T_g values of the pure components. The curves can be fitted to the Gordon–Taylor equation[39] relating the T_g of a blend with those of the pure components

$$T_g=\frac{w_1T_{g1}+kw_2T_{g2}}{w_1+kw_2} \tag{7}$$

where w_i and T_{gi} represent the weight fractions and the glass transition temperatures of the blend components and k is defined by $\Delta\alpha_2/\Delta\alpha_1$, where $\Delta\alpha$ represents the difference in the volume expansion coefficients between the liquid and glassy states. In the absence of the $\Delta\alpha$ data k has been used here as an adjusting parameter.

As can be seen from *Figures 4* and *5* a good fit to the Gordon–Taylor equation is achieved with $k=0.193$ for PVME–PVPr and $k=0.129$ for PVME–PVBu. These best k values were arrived at by following the method of Prud'homme *et al.*[40,41]. Rearranging the Gordon–Taylor equation one obtains

$$T_g=T_{g1}+kw_2(T_{g2}-T_g)/w_1 \tag{8}$$

Thus, by plotting T_g against $w_2(T_{g2}-T_g)/w_1$ the value of k was obtained as the slope of the line that gave the best fit. The value of k has been used as an index of the strength of interaction between the polymer components in the blend[40,41]. For a value of $k=1$ equation (7) gives rise to the weight-average T_g equation

$$T_g=w_1T_{g1}+w_2T_{g2} \tag{9}$$

Table 1 Characteristic parameters of polymer and probes at 25°C

Compound	P^* (J ml^{-1})	V^* (ml g^{-1})	T^* (K)
PVME[a]	518.5	0.8045	6584.3
Ethyl acetate[b]	424.3	0.848	4467.1
Ethyl propionate[b]	411.8	0.873	4675.4
Ethyl butyrate[b]	406.5	0.887	4734.0

[a] From ref. 37

[b] Calculated using equations (4) to (6) with α data at 25°C obtained from refs 32 and 34. P^* was calculated using the relation $P^*=\delta^2\tilde{V}^2$, where δ is the solubility parameter which was calculated following the method of Hoy[38]

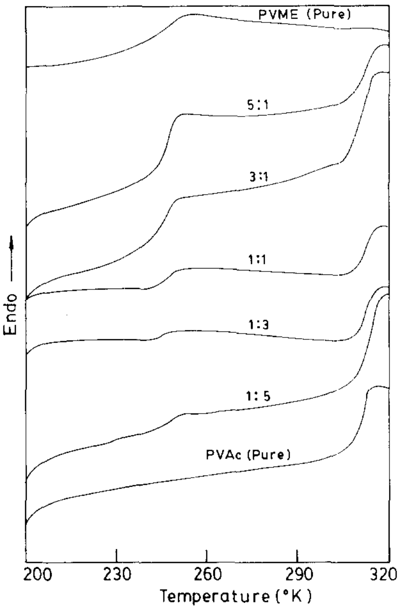

Figure 1 The d.s.c. traces of pure polymers PVME and PVAc (l) and their blends. Blend compositions PVME:PVAc (w/w) are shown

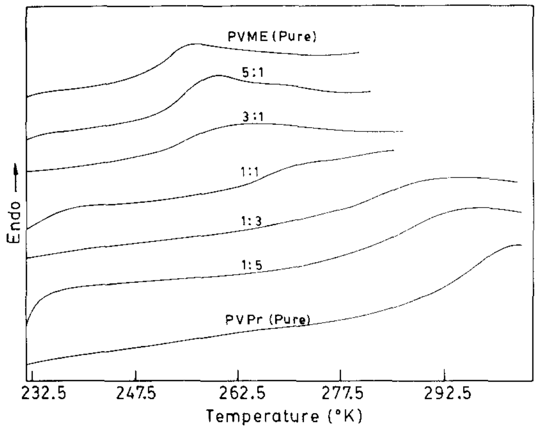

Figure 2 The d.s.c. traces of pure polymers PVME and PVPr and their blends. Blend compositions PVME:PVPr (w/w) are shown

Table 2 Thermodynamic quantities of interaction for the probe (1)–PVME (2) system

Probe	60°C χ^*_{12}	60°C X_{12} (J ml^{-1})	80°C χ^*_{12}	80°C X_{12} (J ml^{-1})	100°C χ^*_{12}	100°C X_{12} (J ml^{-1})	120°C χ^*_{12}	120°C X_{12} (J ml^{-1})	Average X_{12} (J ml^{-1})
Ethyl acetate	0.434	6.87	0.386	3.95	0.395	3.41	0.365	0.96	3.79
Ethyl propionate	0.314	2.54	0.284	0.53	0.264	−1.23	0.245	−3.18	−0.335
Ethyl butyrate	0.234	−0.77	0.234	−1.76	0.194	−4.28	0.184	−5.81	−3.16

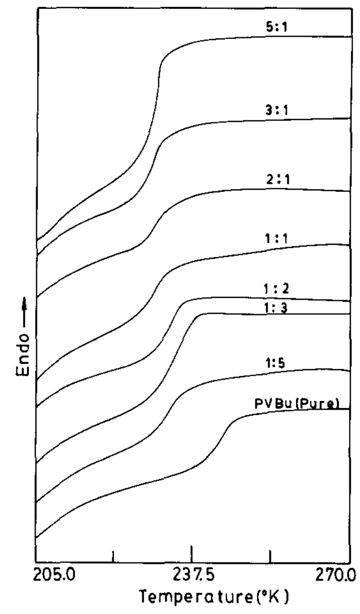

Figure 3 The d.s.c. traces of pure polymer PVBu and PVME–PVBu blends. Blend compositions PVME:PVBu (w/w) are shown

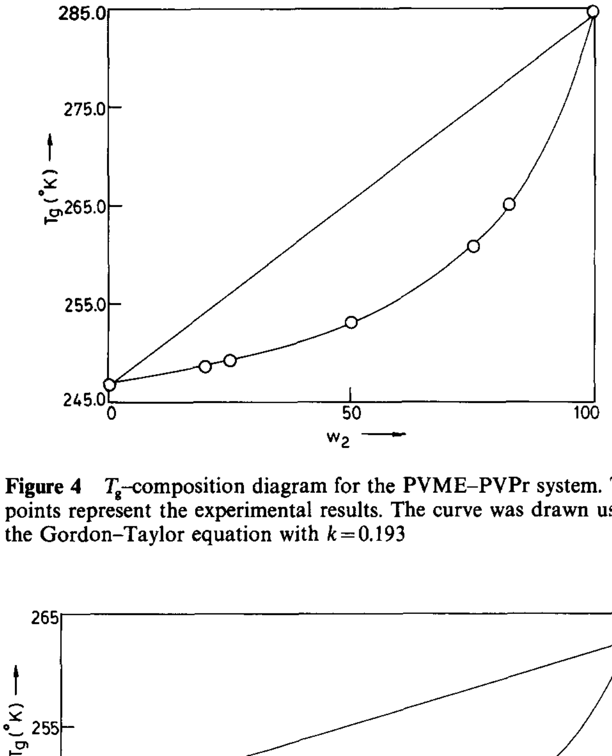

Figure 4 T_g–composition diagram for the PVME–PVPr system. The points represent the experimental results. The curve was drawn using the Gordon–Taylor equation with $k=0.193$

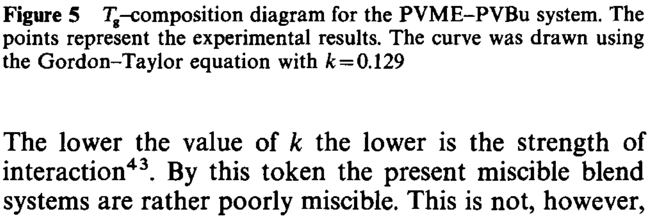

Figure 5 T_g–composition diagram for the PVME–PVBu system. The points represent the experimental results. The curve was drawn using the Gordon–Taylor equation with $k=0.129$

The lower the value of k the lower is the strength of interaction[43]. By this token the present miscible blend systems are rather poorly miscible. This is not, however, supported by the d.s.c. traces. Poorly miscible systems should have yielded heat capacity changes over a very broad range[42–45], which is not found for the present systems (*Figures 2* and *3*).

The X_{12} values and the miscibility prediction

The χ^*_{12} and X_{12} values for the interaction of the three probes ethyl acetate, ethyl propionate and ethyl butyrate with segments of PVME are given in *Table 2* for four temperatures (60, 80, 100 and 120°C). These probes are the hydrogenated monomers for the vinyl ester polymers and used as models to represent the segments of the corresponding polymers. The values of the characteristic parameters P^*, V^* and T^* used in this work for the evaluation of X_{12} from χ^*_{12} using equation (3) are given in *Table 1*. A perusal of the data given in *Table 2* reveals that X_{12} for ethyl acetate–PVME is positive at all the four different temperatures of study. This result contradicts those of Klotz *et al.*[20] who reported a negative value for X_{12} ($-8.76\,\mathrm{J\,ml^{-1}}$).

For the ethyl propionate–PVME and ethyl butyrate–PVME interactions we see from *Table 2* that the X_{12} values for the former system are slightly positive at 60 and 80°C but negative at the other two higher temperatures; for the latter system X_{12} is negative at all four temperatures. For all three blend systems the X_{12} values decrease with increasing temperature. We believe that this trend is not real and may reflect a systematic error. In reality, X_{12} should have been independent of temperature. We are inclined to believe that the temperature variation of X_{12} as reported here is a reflection of the inaccuracy of i.g.c. We therefore averaged the values of X_{12} over the four temperatures. The averages turn out to be as follows: X_{12} is positive for the ethyl acetate probe but negative for the other two probes, i.e. ethyl propionate and ethyl butyrate. These results immediately suggest that PVME would be miscible with PVPr and PVBu but not with PVAc. The miscibility results, as established from the film clarity and glass transition temperature measurements discussed earlier in this work, agree with this prediction.

It may be remarked here that in view of the approximate nature of the X_{12} values (due to the inherent inaccuracy in i.g.c. and the uncertainty in the values of the characteristic parameters), miscibility prediction by the present method should have greater freedom on the sign of the X_{12} values. Not only should the systems with negative X_{12} values give good clues in the search for new miscible polymers, but a search based on systems with small positive X_{12} values may also be rewarding.

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