

The miscibility of polyacrylates and polymethacrylates with PVC: An interpretation of the heats of mixing of oligomers

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Oligomers of various polyacrylates and polymethacrylates and a chlorinated paraffin (as an analogue for PVC) were studied in order to give information relevant to the miscibility of the respective polymers. The heats of mixing of the oligomers with the chlorinated paraffin were measured and showed that those oligomers with the lowest and highest ester group concentration (poly(methyl acrylate) and poly(octadecyl methacrylate)) had unfavourable (positive) heats of mixing whereas oligomers with intermediate ester group concentrations had favourable (negative) heats of mixing. This was consistent with the miscibility of the respective polymers in most cases. The results were interpreted in terms of the summation of the effects of the specific interactions and the dispersive forces. A high concentration of interacting groups leads to a high contribution from the specific interaction, but in the case of poly(methyl acrylate) with the highest concentration of interacting groups this is outweighed by a large unfavourable contribution from the dispersive forces.

Keywords Miscibility; compatibility; heat of mixing; calorimetry; poly(vinyl chloride); polyacrylate; polymethacrylate; solubility parameter

INTRODUCTION

In previous papers¹⁻⁴ we have established the miscibility of PVC with polyacrylates and polymethacrylates with ester side chains of up to 4 and 6 carbon atoms long respectively. There is, however, one probable exception to this rule, poly(methyl acrylate). The miscibility of various polymers which contain ester groups has been attributed to a weak hydrogen bond between the two polymers^{5,6}. It is therefore expected that as the ester side chain increases in length, the concentration of ester groups in the polymer will decrease, and the polymers will become less miscible with PVC. It is not, however, quite so obvious why poly(methyl acrylate), the polymer with the highest concentrations of interacting groups, should be immiscible with PVC.

A recent study of blends of PVC with a range of polyesters by Ziska, Barlow and Paul has shown a similar result⁷. The polyesters are broadly comparable with the polyacrylates except that the ester group lies in the main chain. Owing to the greater symmetry, many of them are also crystalline. They found that poly(β -propiolactone), poly(ethylene succinate) and poly(ethylene adipate) were not miscible with PVC whereas homologues with a lower ester group concentration from poly(butylene adipate) to poly(hexamethylene sebacate) were miscible. They calculated the interaction parameters from the melting point depression data and found that those with the lowest concentration of ester groups had the most favourable (negative) values. They pointed out that this trend must be reversed since PVC is certainly not miscible with polyethylene. It has also been noted⁸ that similar

ethylene/carbon monoxide copolymers are immiscible with PVC at 14 wt% CO but miscible at 15 wt% CO. Obviously there is a minimum necessary concentration of interacting groups. In particular it is interesting that the lower limit of miscibility in their systems coincides with that in the polyacrylates, four CH₂ (or CH₃, etc.) groups for each C=O group, and that the least polar polyester they consider still has less CH₂ (or CH₃, etc.) groups for each C=O than poly(hexyl methacrylate).

It is our intention to explain this effect semiquantitatively in terms of the summation of the (favourable) specific interactions and the normal (unfavourable) dispersive interactions within the systems.

We have in a previous paper² described the determination of the interaction parameters between the polyacrylates and PVC by inverse gas chromatography. However, this technique cannot be used to give information concerning systems which cannot be solvent cast to give a one-phase blend⁹. For reasons discussed elsewhere¹⁰ we also do not consider this a reliable method for the quantitative determination of interaction parameters.

Interaction parameters can also be determined from the heat of mixing (ΔH_m) from

$$\Delta H_m = K T n_1 \phi_2 \chi_{12}$$

where n_1 is the number of molecules of component 1 and ϕ_2 the volume fraction of component 2. It should be noted, however, that such values are not strictly comparable with those determined from inverse gas chromatography as they are purely due to the exchange energy

whereas the latter also contain contributions from any non-combinatorial entropy changes. The enthalpy of mixing of two high molecular weight polymers cannot be determined directly due to the low diffusion coefficients of large molecules. This difficulty can be overcome by using low molecular weight analogues or oligomers.

In this work we have determined the heats of mixing of a range of oligomeric analogues of polyacrylates and PVC and made an estimate of the dispersive interactions using solubility parameter data in order to obtain an estimate of the various contributions to the free energy of mixing.

EXPERIMENTAL

Materials

The monomers methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate (octyl acrylate), methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate and octadecyl methacrylate were obtained commercially. They were purified by washing twice with aqueous sodium hydroxide solution (10% w/v) to remove inhibitor and then with distilled water. They were then dried over anhydrous calcium chloride for 48 h and distilled under reduced pressure.

Oligomers were prepared by a solution polymerization technique similar to that used by Shimomura¹¹. A typical preparation uses inhibitor-free monomer (1 mole), isopropanol (30 mole, chain transfer agent, A.R.) and azobisisobutyronitrile (0.15 mole, initiator). The materials were introduced into a flask and nitrogen was bubbled through for 10 min to remove dissolved oxygen. The mixture was heated and stirred under reflux for 12 h. The solution was cooled, filtered and evaporated to dryness. The viscous oligomers were then dried in a vacuum oven at 50°C and 1 mm Hg for two weeks. Details of the preparations are shown in Table 1. It should be noted that the oligomers will contain a fairly high proportion of end groups and initiator fragments which will make them imperfect analogues for the high molecular weight polymers.

A commercial oligomeric chlorinated paraffin (Cereclor S52, I.C.I.) was used as an analogue for PVC. It contained 53.1% w/w chlorine (the figure is 56% for PVC). The distribution of chlorines will also not be identical to PVC but two substitutions onto one carbon will not be preferred.

The molecular weights of the various oligomers were

determined by g.p.c. (in THF as a solvent, relative to polystyrene standards) or by vapour-phase osmometry (at 37°C using butan-2-one as a solvent). The results are shown in Table 1.

Measurement of heats of mixing

A modified NBS batch-type microcalorimeter¹² was used for the measurements. Measurements were made at 70°C. A total of 1.5 g of the oligomeric samples of polyacrylate and chlorinated paraffin in the correct ratio were weighed into the separate cell compartments and after equilibration at the temperature of measurement the samples were mixed. The machine was calibrated by passing a current through the mixture under investigation. The machine has an accuracy of $\pm 0.02 \text{ J g}^{-1}$ determined by acid-base reactions; however, the viscosity of the oligomers made mixing difficult. Repeated runs gave ΔH values which were reproducible within $\pm 0.1 \text{ J g}^{-1}$.

RESULTS AND DISCUSSION

The heats of mixing over a range of compositions have been measured for oligomers of poly(butyl methacrylate), poly(hexyl methacrylate), poly(methyl acrylate) and poly(butyl acrylate) with Cereclor S52. The results are shown in Figure 1. The values are negative at all compositions except in the case of the poly(methyl acrylate). It should be noted that this polymer was found to be immiscible with PVC. The asymmetry in the curves cannot be put down to experimental error.

The remaining five oligomers were only measured for 50:50 w/w mixtures. We have calculated the weight fractions of carbonyl groups ($W_{\text{C=O}}$) in each of the polymers and have plotted this against the heats of mixing. The results in Figure 2 show that the heats of mixing are most favourable for intermediate values of $W_{\text{C=O}}$ and become unfavourable at higher and lower values.

The heats of mixing can be represented as due to two contributions, the specific interactions, which should depend on the concentration of interacting groups, and the dispersive forces. The latter can be given in terms of the solubility parameters of the two components δ_1 and δ_2 as:

$$\Delta H_{\text{dispersive}} = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

where V_m is the total volume of the system.

Table 1 Preparation and properties of oligomers

Oligomer	Preparation			\bar{M}_n^*	\bar{M}_w^*
	Monomer (ml)	Isopropanol (ml)	Initiator (g)		
Poly(methyl acrylate)	50	1000	19	646	928
Poly(ethyl acrylate)	50	900	13	744	1508
Poly(butyl acrylate)	50	700	10	983	1940
Poly(octyl acrylate)	50	490	7	1020	2800
Poly(methyl methacrylate)	50	900	13	434 [†]	—
Poly(ethyl methacrylate)	50	790	11.5	722	1440
Poly(butyl methacrylate)	50	633	9	890	2220
Poly(hexyl methacrylate)	50	529	7.7	898	2127
Poly(octadecyl methacrylate)	50	276	4	925	1730
Cereclor S52		^a		437 [†]	

* By g.p.c. relative to polystyrene standards

† By vapour-phase osmometry

^a Supplied by I.C.I.

Values of δ can be obtained from the literature¹³. Where this is not available, values of δ can be calculated using Small's group contribution method, as tabulated by Van Krevelen¹⁴. The results are shown in Table 2. The calculated values of $\Delta H_{\text{dispersive}}$ have been plotted against $W_{C=O}$ for the series of polymers as shown in Figure 3. This gives a typical U-shaped curve. The contribution to ΔH is always positive (unfavourable) and tends to zero as the solubility parameters of the two polymers become more nearly equal. The polyacrylates and polymethacrylates will not have identical calculated δ values for a given $W_{C=O}$ but the difference is small and has been ignored.

The contribution to ΔH from the specific interactions can be deduced from the difference between the experimental curve shown in Figure 2 and the dispersive contribution calculated from the data in Table 2 and shown in Figure 3. The resulting values are also shown in Figure 3. There is quite a lot of scatter, which is not surprising considering the assumptions made, but the results clearly show that a larger contribution to the heats of mixing is given by those polymers with a higher

concentration of interacting groups. The poly(methyl acrylate) has a high contribution from the specific interactions but this is outweighed by a very large unfavourable dispersive interaction.

In considering the scatter in this plot one must also bear in mind that different carbonyl groups may not have identical capacities for interaction. Differences could arise from inductive effects altering the strengths of the interaction and from steric effects altering the accessibility of the interacting groups. The treatment should therefore only be considered as giving a qualitative overall picture, in which respect it is very successful, and not as a quantitative measure of the interaction.

Correlation with polymer miscibility

When comparing these heats of mixing with the compatibilities of the respective polymers and PVC one can see some correlations. They explain the immiscibility of poly(methyl acrylate) with PVC and the immiscibility of very long side chain polyesters with PVC. This simple treatment, however, suggests that poly(octyl acrylate) should be miscible when in fact it is not. It also would

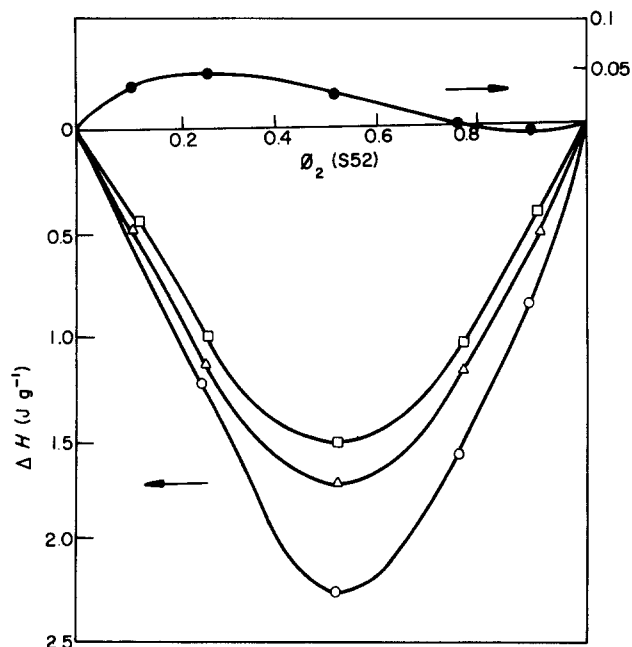


Figure 1 Heats of mixing at different volume fractions of Cereclor S52 with poly(methyl acrylate) (●), poly(butyl acrylate) (○), poly(hexyl methacrylate) (△) and poly(butyl methacrylate) (□)

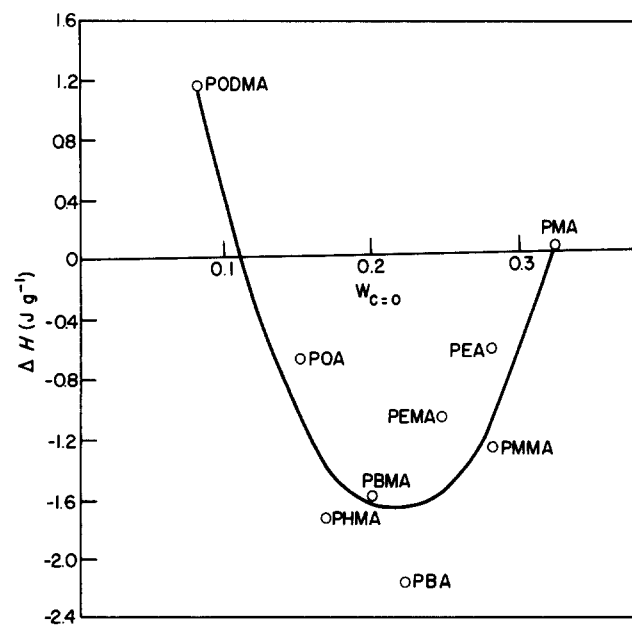


Figure 2 The heats of mixing of various oligomeric polyacrylates and polymethacrylates with Cereclor S52 (an analogue for PVC), at 50:50 w/w, plotted against weight fraction of carbonyl groups in the copolymers

Table 2 Data used for the calculation of the heats of mixing

Material	Density (g cm ⁻³)	$W_{C=O}$	Mixture volume* (cm ³ g ⁻¹)	ϕ_2	ϕ_1	δ_1 (J cm ⁻³) ^{1/2}	$(\delta_1 - \delta_2)^2$ [†] (J cm ⁻³)	ΔH_{disp} (J g ⁻¹)	δH_{sp} [‡] (J g ⁻¹)
PMA	1.22	0.325	0.8170	0.4984	0.5016	20.7	11.56	2.36	-2.22
PEA	1.10	0.28	0.8617	0.4725	0.5275	19.2	3.61	0.78	-1.42
PBA	1.055	0.219	0.8811	0.4621	0.5379	18.0	0.49	0.11	-2.38
POA	0.927	0.152	0.9464	0.4302	0.5698	17.2	0.01	0.002	-0.74
PMMA	1.18	0.28	0.8390	0.4900	0.5100	18.6	1.69	0.36	-1.65
PEMA	1.11	0.246	0.8576	0.4748	0.5253	18.4	1.21	0.26	-1.34
PBMA	1.055	0.197	0.8811	0.4621	0.5379	17.9	0.36	0.08	-1.70
PHMA	1.04	0.165	0.8879	0.4586	0.5414	17.6	0.09	0.02	-1.79
PODMA	0.85	0.083	0.9954	0.4145	0.5855	15.6	2.89	0.70	+0.45

* In this case the mixture volume is the specific volume in order to obtain ΔH in J g⁻¹

† Using $\delta_2 = 17.3$

‡ Calculated from ΔH_{total} in Figure 2 and ΔH_{disp}

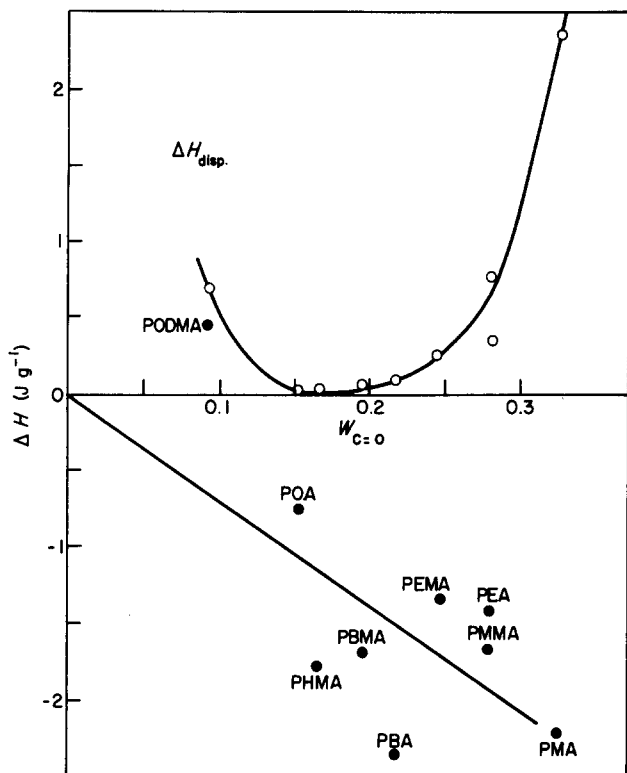


Figure 3 The contributions to the heats of mixing of various oligomeric polyacrylates and polymethacrylates with Cereclor S52 from the dispersion forces (○) calculated from solubility parameters and the specific interactions (●) calculated as the difference between the former and the total shown in Figure 2, plotted against the weight fraction of carbonyl groups in the polymers

suggest that poly(butyl acrylate) and poly(hexyl methacrylate) should be among the polymers with the most favourable interactions with PVC. In fact we know that these two polymers phase separate from PVC on heating though this could be explained by a strong temperature dependence of the interaction.

This picture, of course, ignores other contributions to the free energy of mixing, the combinatorial entropy, the contribution from the equation-of-state terms and the contribution from the non-combinatorial entropy of mixing. The first two should be quite small compared with the ΔH values but the third can be large in systems with strong specific interactions.

Other problems may arise because of the simplifications inherent in the use of solubility parameters and from differences between the polymers and their oligomeric analogues. In particular the calculated solubility parameter of the Cereclor is 17.3 whereas PVC is normally quoted¹³ at 19.2. If we consider this value we can see that we can explain the immiscibility of poly(octyl acrylate) and the limited temperature range of miscibility of poly(hexyl methacrylate) and poly(butyl acrylate). However, a higher solubility parameter for PVC would suggest that poly(methyl acrylate) should be miscible with it. This could be explained by the presence of a large unfavourable non-combinatorial entropy contribution in this case. If the non-combinatorial entropy is associated with ordering as a result of the specific interaction, then we would expect it to reduce the overall effect of the interaction, which contributes most in the case of polymers with the highest carbonyl group content.

If we compare the values of ΔH with values of the polymer-polymer interaction parameter (χ_{23}) measured

by inverse gas chromatography², or with the Gordon-Taylor parameter (K) which represents the deviations of the glass transition parameters from the weighted means⁴, then the correlations are poor. The latter two are only available for miscible blends, and it is in these blends where the greatest scatter is observed in our results (as shown in Figure 2) and we have not been able to explain the origin of this scatter. Furthermore χ_{23} contains all the non-combinatorial entropy contributions to the free energy and K is basically an empirical parameter since the dependence of T_g on the interactions is not fully understood. We, therefore, do not expect a good correlation.

Finally, we consider the work of Ziska, Barlow and Paul⁷ on the compatibility of polyesters with PVC. A polyester with the same carbonyl group content as a polyacrylate would be expected to have about the same solubility parameter and about the same level of specific interactions. One would therefore expect miscibility in the respective cases and the same overall explanation of the miscibilities would prevail.

CONCLUSIONS

The heats of mixing of oligomeric analogues of various polyacrylates and polymethacrylates with PVC have been found to be consistent in most cases with the miscibility of the respective polymers. Both those with the highest and lowest carbonyl group contents have positive (unfavourable) heats of mixing while the respective polymers do not mix with PVC.

The results have been explained in terms of the contributions to the heats of mixing from the dispersive forces and the specific interactions. The specific interaction must have a sufficient contribution to overcome the unfavourable dispersive forces in order that an overall favourable heat of mixing should result.

The inconsistencies of detail are thought to arise from the assumptions implicit in the use of solubility parameters, from the fact that the oligomeric analogues are not identical to the respective polymers, and from ignoring contributions from the equation-of-state, combinatorial and non-combinatorial entropy to the free energy of mixing.

The explanation is also applicable to the miscibility of various linear polyesters with PVC previously described in the literature.

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